Fractal Properties and Applications of Dendritic Filaments in

Programmable Metallization Cells

by

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ABSTRACT

Programmable metallization cell (PMC) technology employs the mechanisms of metal ion transport in solid electrolytes (SE) and electrochemical redox reactions in order to form metallic electrodeposits. When a positive bias is applied to an anode opposite to a cathode, atoms at the anode are oxidized to ions and dissolve into the SE. Under the influence of the electric field, the ions move to the cathode and become reduced to form the electrodeposits. These electrodeposits are filamentary in nature and persistent, and since they are metallic can alter the physical characteristics of the material on which they are formed. PMCs can be used as next generation memories, radio frequency (RF) switches and physical unclonable functions (PUFs).

The morphology of the filaments is impacted by the biasing conditions. Under a relatively high applied electric field, they form as dendritic elements with a low fractal dimension (FD), whereas a low electric field leads to high FD features. Ion depletion effects in the SE due to low ion diffusivity/mobility also influences the morphology by limiting the ion supply into the growing electrodeposit.

Ion transport in SE is due to hopping transitions driven by drift and diffusion force. A physical model of ion hopping with Brownian motion has been proposed, in which the ion transitions are random when time window is larger than characteristic time. The random growth process of filaments in PMC adds entropy to the electrodeposition, which leads to random features in the dendritic patterns. Such patterns has extremely high information capacity due to the fractal nature of the electrodeposits.

In this project, lateral-growth PMCs were fabricated, whose LRS resistance is less than 10Ω , which can be used as RF switches. Also, an array of radial-growth PMCs was fabricated, on which multiple dendrites, all with different shapes, could be grown simultaneously. Those patterns can be used as secure keys in PUFs and authentication can be performed by optical scanning.

A kinetic Monte Carlo (KMC) model is developed to simulate the ion transportation in SE under electric field. The simulation results matched experimental data well that validated the ion hopping model.

This dissertation is dedicated to my parents and my wife.

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LIST OF TABLES viji
LIST OF FIGURESix
CHAPTER
INTRODUCTION 1
Redox Reaction and Mass Transport in Electrochemical Deposition1
Background of Programmable Metallization Cells
Fractal Properties 4
Mechanism of PMCs
Ion Transport in PMCs10
PMC Applications12
Challenges and Future of PMCs166
PMC BASED IONIC SWITCH 199
Introduction199
Filament Properties Impacting Switching Performance
Device Fabrication
Redox Reactions in PMC 32
Physical Model of Ion Hopping Transitions in PMC37
Electrical Performance of Lateral PMC Switches42

TABLE OF CONTENTS

CHAPTER	Page
Fractal Properties of Filaments	50
Simulation Approach	
DENDRITE PHYSICAL UNCLONABLE FUNCTIONS	75
Introduction	75
Pattern Randomness	75
Device Structures and Fabrication Process	77
Experimental Results	
PUF Application	100
ION HOPPING MODEL AND SIMULATION OF PMC DEVICES	105
Ion Hopping Model	105
Algorithm	107
Hopping Algorithm	113
Application of The Simulation	115
Relationship between Growth Conditons and Fractal Dimensions	115
CONCLUSION	118
REFERENCES	

LIST OF TABLES

Table Page
II.1: List Of All The Input Pulse Configuration Used For Programming The Lateral
PMC Switches
III.1: Information Capacitance Of Radial PMC At Different Resolution When FD Is
1.37 And E ₁ Is ¹ / ₂
V.1: Relationship Between Filaments' Growth Conditions And Fractal Dimensions
With Examples

LIST OF FIGURES

Figure Page
I.1: The Scheme of A Redox Reaction
I.2: Example of Koch Snowflake Fractal Pattern
I.3: Image of Filaments Formed in a Radial PMC
I.4: Demonstration of The Box-Counting Dimension
I.5: The Schematics of PMC Devices. When a Positive Voltage Is Applied on the Anode,
the Metal Ions Will Migrate to the Cathode and Reduce to Form the Filaments 10
I.6: Ion Hopping Barriers in Amorphous Chalcogenide Glass. The Upper Diagram Is the
Equilibrium State That all the Barriers Have the Same Height; The Lower Diagram Is
the Non-Equilibrium State When External Voltage Is Applied That the Barrier Lowers
along the Direction of The Electric Field As the WS Ladder
I.7: The Schematic of a Lateral PMC Device. It Is a Coplanar Structures That Both the
Anode and Cathode Are on the Surface of the Solid Electrolyte13
I.8: The Schematic of a Lateral PMC Based Microfluidic Valve
I.9: The Schematic of a Radial PMC Device16
II.1: A Schematic of the MEMS RF Switch
II.2: Classification of the Filaments in Lateral PMC Devices. The Filaments in the Red Box
Formed outside the Switching Channel Are The Group A Filaments and the Ones in
the Green Box Are The Group B Filaments
II.3: The Layout of the Lateral PMC Switch. Combinations of Different Electrode Width
and Gap Spacing Were Design

II.4 (A)-(L):Shematic of the Fabrication Process of a Lateral PMC Switch
II.5: A Diagram of the Change of Gibbs Free Energy of Metal Ions Upon Formation of a
Nuclei of Radius R
II.6: Calculated Data of Filament Temperature Vs. Filament Resistance During the Erase
Operation and the Erase Voltage Was 3V
II.7: The Relationship of the Gibbs Free Energy between the Metallic and Ionic
Phases
II.8: Electric Field in the Lateral PMC Devices, When 3v Bias Was Applied Across the
Anode and Cathode and the Strongest Electric Field Occurred at the Electrodes Corners.
Simulated by Comsol Multiphysics
II.9: A Schematic of Brownian Motion
II.10: Image of Fabricated Device: (A) the View of the Entire Device; (B) the Zoomed-in
View of the Switching Area
II.11: The Switching Curve of a Lateral PMC Switch
II.12: HRS and LRS of a Lateral PMC Switch
II.13 (A)-(D): The SEM Image of the PMC Switch after Programming
II.14: Schematic of the Lateral Pmc Switch With Thick Alumina Contact Layer 489
II.15: HRS and LRS of a Lateral PMC Switch With Aluminum Contact
II.16: Input Pulse Configuration for Programming the Switch
II.17: A Typical Electroforming Curve Of The Lateral Pmc Switch

II.18: Image of Dendritic Filaments Formed in a Lateral PMC Switch. The Stage 1
Filaments Are Small Dense Filaments Formed Near the Cathode and The Stage 2
Filaments Are More Linear and in Larger Size
II.19: Fractal Dimensions of Stage 1 and 2 Filaments Formed under All the 16
Programming Configuration
II.20: The Ratio of Group B Filaments under Different Growth Conditions
II.21: Filaments Formed under All This 16 Growth Conditions
II.22: (A) When Ion Is Depleted inside the Switching Channel, Almost Only the Ions
outside the Switching Channel Will Contribute to the Filament Growth; (B) When an
Ion Moves Close to the Cathode, It Gets Captured by the Electric Field; (C) the Ion
Moves along the Electric Field; (D) the Ion Reaches the Cathode Corner and Gets
Reduced There
II.23: The SEM Images of the Switching Channel in the Lateral PMC Device with Some

 Ag Dendrites (Filaments) Formed at the Cathode. The EDS Measurements Were

 Applied along These Two Magenta Dash Lines and the Plots on the Right Show the

 Results That the Ag Concentration outside the Switching Channel Was Quite

 Uniformed, While the Concentration Decreased Near the Anode inside the Switching

 Channel.

 62

 II.24: Structure of Lateral PMC Switch Used in the KMC Model.

 63

 II.25: Simulated Filaments with the Growth Condition of 3v, 0.3s PW and 3s PI. Like the

 Experimental Filaments, It Comprises Stage 1 and Stage 2 Filaments As Well.

- II.28: (A) Simulated Filaments with the Growth Condition of 3v, 0.3s PW and 1s PI; (B)
 Simulated Filaments with the Growth Condition of 3v, 0.3s PW and 10s PI; (C)
 Experimental Filaments with the Growth Condition of 3v, 0.3s PW and 1s PI; (D)
 Experimental Filaments with the Growth Condition of 3v, 0.3s PW and 1s PI; (D)
 Experimental Filaments with the Growth Condition of 3v, 0.3s PW and 1s PI; (D)

III.3: The Layout of Three Radial PMC Arrays with Different Diameters. (A) $200\mu m$
Diameter; (B) 800 µm Diameter; (C) 2400 µm Diameter
II.4: The Photo of the Die of the Radial PMC Array. The Anode and Cathode Are the
Indicated Spots
III.5: Image of the Radial PMC Array That Filaments Were Formed Simultaneously 86
III.6: Filaments Formed under Different Growth Voltage. (A) 2v; (B) 1v
III.7: Dendrite Formed in Different Type Devices with the Same Growth Voltage (2v): (A)
Type A Device (200 µm Diameter); (B) Type B Device (800 µm Diameter)
III.8: Schematic of the Ion Transportation during the Growth
III.9: Light Path of the Microscope: (A) Bright Field; (B) Dark Field
III.10: Bright Field (Left) and Dark Field (Right) Image of the Dendrites. Upper Images
Are Type A Device Programmed with 1v; Middle Images Are Type A Device
Programmed with 2v; Lower Images Are Type B Device Programmed with 2v 92
III.11: Bright Field (Upper) and Dark Field (Lower) Images of the Type 2 Device Dendrite.
The Morphology of the Dendrite Transited When Getting Close to the Anode As
Marked in the Green Box
III.12: Image of Dendrites Acquired by Optical Prolifilometer: (A) Top View; (B) Side
View
III.13: Height Measurement on a Crossection of the Dendrite
III.14: AFM Results of the Dendrites
III.15: (A) Bright Field Image of the Dendrite; (B) Binary Image Converted from (A) with
Matlab Image Process Toolbox That Was Ready for FD Analysis

III.16: Statistic Results of FD and Pattern Size of the Dendrites Formed Simultaneously.
III.17: Micrograph of a Radial Silver Dendrite (Top) Illustrating Fractal Branching at
Decreasing Scale (Bottom Images). The Yellow Dots Are The Branching Points and
the Yellow Arrows Indicate the Main Branches
III.18: Schematic of the Binary Information of Dendrites. The Pattern Is Converted As a
Pixel Matrix and the Locations with the Presence of Dendrite Are Marked As "1" and
the Rests Are Marked As "0"
III.19: Features on Dendrites Extracted by Sift Process with Imagej
IV.1: Schematic of an Ag Ion Moving to the Filament under a Relatively Low Voltage. the
Ion Is Reduced before Reaching the Filament Tip107
IV.2: The Schematic of Matrix in KMC Model Representing a Radial PMC 108
IV.3: The Polar Coordinate System in the Matrix
IV.4: The Formation of Dendrites Consumes Silver Ions in Chalcogenide and Leads to a
Silver Depletion Region As Marked by the Dashed Circle
IV.5: Scheme of the Drift and Diffusion Orientation after Forming Trunks of Dendrites.
IV.6: Scheme of the Brownian Motion in the Kmc Model. The Red Pixel Is the Position of
the Silver Ion, Which Has a Probability Y to Move to Any of the Yellow Pixels 111
IV.7: Schematic of the Reduction Judgement in the KMC Model. When the Ion Move to a
Pixel Next to the Dendrites, It Gets Reduced
IV.8: Simulation Results with Different Voltage: (A) Low Voltage; (B) High Voltage.113

IV.9: Hopping Approach in the KMC Model. The Red Pixel Could Randomly Move to
Any of the Hopping Site (Yellow Pixels) within a Wiggle Angle B 114
IV.10: Simulated Dendrites with Same Parameters
IV.11: Dendrite Patterns Generated by the KMC Simulator with Low (Left) and High
(Right) Electric Field 115
IV.12: Simulated Dendrite Patterns with Different Anode Supply: (A) High Anode Supply;
(B) Medium Anode Supply; (C) Low Anode Supply116

Chapter 1

INTRODUCTION

REDOX REACTIONS AND MASS TRANSPORT IN ELECTROCHEMICAL DEPOSITION

Electrochemical deposition has developed into an important process in the electronics industry. For example, electroplating has been used to make copper interconnects in integrated circuits (ICs) for many years. The first patent of electrochemical deposition dates back to 1840 [1], which is regarded as the beginning of the electroplating industry [2]. The early usage of electroplating included making mirrors, decorating tableware and delivering special physical or mechanical properties (corrosion resistance, electrical conductivity, lubrication, etc.) to the surface of cheaper substrates. In the 1960s, the electronic industry began to use electrochemical technology to manufacture printed circuit boards (PCBs) and in 1998, a revolution started in the IC industry in which aluminum interconnects fabricated by sputtering were replaced by copper interconnects manufactured by electrodeposition [3].

Electrodeposition involves both the electrical and chemical changes in which atoms lose electrons in the process of oxidation at an anode and to create ions which are able to move under an electric field in electrolytes. On receiving electrons from a cathode, ions are reduced back to atoms which are immobile in the field in the process of reduction. Both of these processes together constitute redox reactions which is the key to electrodeposition. Figure I.1 shows a schematic representation of a redox reaction, in which the anode is made of an electrochemically active metal and the electrolyte is a liquid or solid solution which the anode ions can dissolve into. In this situation, the anode atoms move under the electric field resulting in the redistribution of mass from the anode to the cathode [4]. This process will only occur when sufficient positive bias is applied on an active anode against a cathode. Typically, the bias should be higher than a few hundred millivolts [5], so that the chemical potential barrier at the anode can be overcome. There are two types of current flows in this process: the one associated with the movements of metal ions is non-faradic; the one associated with the redox reactions is faradic. The total amount of the faradic charge (the electrons provided by the external circuit at the cathode) determines the number of atoms depositing at the cathode. Therefore, the total electrodeposited mass is controlled by the power supply of the external circuit [6]. Moreover, the electrodeposition process is reversible if the cathode is electrochemically inert that when reverse bias is applied, the deposited metal atoms at the original cathode will get oxidized, dissolve into the electrolyte and transport back to the original anode. Similarly, these ions will be reduced and deposited at the original anode. This process will terminate by itself when all the electrodeposited metal has been dissolved. Thus, the asymmetric structure with an electrochemically active anode and inert cathode enables repeatable cycles of the electrodeposition and dissolution.



Figure I.1: The schematic of a redox reaction.

BACKGROUND OF PROGRAMMABLE METALLIZATION CELLS

The Programmable Metallization Cell (PMC) device is receiving increasingly more attention, since it can be used in conductive-bridging RAM (CBRAM) [7, 8], RF switches [9], and microfluidic valves [10]. The mechanism of PMCs is the formation and annihilation of the electrodeposit via electrochemical redox reactions. The electrodeposit in PMCs is called the metal filament, which connects the anode and cathode creating a low-resistance state (LRS) from an initial high-resistance state (HRS) [11, 12]. In most research, the filaments are regarded as lines or truncated cones neglecting the fractal structures. For example, the filaments in CBRAM are usually treated as truncated cones for which the only important factor is whether the filaments are connecting the electrodes [7]. This approximation is acceptable because CBRAMs are digital devices that the tolerance in LRS

and HRS can be large, which means the filament shape is not important, as long as the HRS and LRS are distinguishable.

Many experimental and simulation studies on CBRAMs have been performed to explore the relationship between filament growth conditions and device performances [13-16]. Also the rough shapes of filaments have been observed and simulated, in order to develop the relationship between device mechanisms and filament formation [16-18]. However, in most of the research work, the filaments were treated as Euclidean geometries for the convenience of calculation and studies on fractal properties of the filaments are still lacking.

For non-digital applications, the fractal structures may be critical. First of all, the fractal structures cause different contacting area on the anode, which impacts the device performance significantly, including the resistance and stability of the LRS and the power required to erase the device [7, 19, 20]. Also, the applications of the filament patterns themselves is promising in the area of physical unclonable function (PUF) applications.

FRACTAL PROPERTIES

Self-similarity means the whole pattern of an object is similar to any part of it. The Koch snowflake is an ideal example of self-similarity, as Figure I.2 shows. Figure I.2 (a) is an equilateral triangle, which can transform to a hexagram as Figure I.2 (b) shows by adding an equilateral triangle to each side of the original triangle and it can further transform to (c), (d) and so on. Unlike the Koch snowflake, a pattern of real filaments is not exactly similar to any part of it, but it still has something of a self-similar property as Figure I.3 shows. Essentially, filaments are not simple lines because finer structures can be

always observed under higher magnification. As mentioned in above, these fine structures play important roles in PMCs, since they actually contact the anode that determines the resistance of the LRS. Moreover, the information that can be represented by such fine structures can be used as PUFs with an appropriate encoding algorithm.



Figure I.2: Example of Koch snowflake fractal pattern.



Figure I.3: Image of filaments formed in a radial PMC.

A critical fractal property is the fractal dimension [21] (FD), which is used to describe the complexity of a fractal pattern. With a higher FD, the pattern is more complicated and denser. Thus, the morphologies of filaments may vary if their FDs are different. Mathematically, the definition of the fractal dimension D is

$$\mathbf{D} = -\log_{\mathbf{G}} N \tag{I.1},$$

where ε is the scaling factor and N is the number of iterations. In the example of figure I.2, the scaling factor is 1/3 and number of iterations is 4, so D equals 1.26. This fractal dimension is also named as Hausdorff dimension [22-25], which is usually used for ideal cases. However, in a real PMC electrodeposit, the shapes of filaments are usually irregular and therefore cannot be readily calculated as a Hausdorff dimension. To obtain these fractal

dimensions, an approximate method called box counting is widely used, which leads to the Minkowski dimension [25-27]. It is defined as

$$D_{bc} = \lim_{\epsilon \to 0} \frac{\log N(\epsilon)}{\log(1/\epsilon)}$$
(I.2),

where D_{bc} is the box counting fractal dimension, \in is the side length of a box which is a unitless number and N is the number of boxes covering the pattern. For example, figure I.4 shows the box-counting with three different box sizes on a regular fractal shape. In the top one, \in is 1/3 and N is 3, so D is 1; in the middle one, \in is 1/9 and N is 12, so D is 1.13; in the bottom one, \in is 1/27 and N is 48, so D is 1.17. Moreover, the expression of N (\in) is

$$N(\epsilon) = 3 * 4^{\frac{\log 1/\epsilon}{\log 3} - 1}$$
(I.3),

Substituting this expression into expression I.2, the Minkowski dimension of this Koch snowflake pattern is 1.26, which matches the Hausdorff dimension well. However, in many practical cases, the limit of expression I.2 may not exist since the box size cannot be infinite small. Instead, it will have a limit superior and a limit interior which refer to the upper and lower box-counting dimensions can be. It reveals the instability of the box-counting dimension, but as long as the box size is small enough and the same parameters are applied for all the measurements, either the upper or lower box-counting dimension could be used to describe the fractal dimension of a real object. Besides FD, there are other filament properties such as area ratio and maximum length and these are discussed in the following chapters.



Figure I.4: Demonstration of the box-counting dimension. MECHANISM OF PMCS

A PMC device contains an electrochemically active anode, like silver (Ag) or copper (Cu) and an inert cathode, like nickel (Ni) or platinum (Pt). The anode and cathode are connected with a thin layer of electrolyte, usually made of chalcogenide or oxides glasses, in which the anode metal ions can dissolve and migrate via drift or diffusion. PMC devices can be designed as vertical, parallel (lateral), or radial structures. The vertical structures are widely used in non-volatile memories, which are also known as CBRAMs [28]; the lateral structures are generally used in RF switches due to the low insertion loss and small off-state capacitance [9]; the radial structures can be used as PUFs due to the high information capacity and resistance to optimal attacks. Whatever the device structure is, the mechanisms of the electrochemical redox process are the same.

Figure I. 5 is a schematic of a vertical PMC. When a positive voltage is applied on the anode opposite to the cathode, the atoms in the anode will be oxidized to ions and dissolve into the electrolyte. Under the influence of the electric field, these ions will drift towards the cathode and become reduced. As a result, the reduced anode metal will accumulate at the edge of the cathode and grow towards the anode until a conducting bridge of the electrodeposit is formed. This conducting bridge shorts the device and sets it to the LRS. The conducting bridge is usually filamentary and this operation is called "write" or "program". To reset the device, a reverse bias needs to be applied, which will generate a temperature rise due to Joule heating and break the weak points on the filaments. Afterwards, the atoms in the filaments will get oxidized into ions and move back to the anode to eliminate the conducting bridge and brings the device back to the HRS. As the cathode is electrochemically inert, the redox reactions are terminated when all the atoms in the filaments are oxidized. This operation is called erase [9, 29].



Figure I.5: The schematic of a vertical PMC device. When a positive voltage is applied on the anode, the metal ions will migrate to the cathode and be reduced to form the filaments.

ION TRANSPORT IN PMCS

The main mechanisms of ion transport in SEs such as chalcogenide glasses are drift and diffusion via correlated hopping transitions [14, 30-34], which are thermally activated transport processes. Usually, hopping refers to the electron transport in narrow-band semiconductors but in SEs, the ions have the similar behavior. The chalcogenide glass films in PMCs are amorphous and contain many voids where metal ions can reside and move. Those ions can bond with the glass creating potential wells, which are the hopping sites. The voids can help with the ion transport and filament formation within an electrolyte. In the equilibrium state, all the barriers are of similar height as the upper diagram of figure I.5 shows, so these is the same probability for an ion hopping from site A to site B as from site B to site A. When an external voltage is applied, the barriers lower along the electric field and this raises the probability of hopping in the direction of the field. This barrier lowering effect is called Wannier-Stark ladder (WS ladder) [35].

In most PMCs, the chalcogenide layers are highly doped with the anode metal in order to supply ions for the growth of the filaments, and the initial distribution of the ions is almost uniform. The ion concentration will decrease during the formation of the filaments, if the ion supply rate by the anode is slower than the uptake rate by filament formation. For lateral PMC devices, the size of the filaments is typically so large that the consumption of the pre-doped ions creates a chemical gradient from the anode to cathode. As a result, the metal ions diffuse into the chalcogenide from the anode. More details about the ion drift and diffusion are discussed in Chapter II and III.



Figure I.6: Ion hopping barriers in amorphous chalcogenide glass. The upper diagram is the equilibrium state that all the barriers have the same height; the lower diagram is the non-equilibrium state when external voltage is applied lower the barriers along the direction of the electric field as in the WS ladder.

PMC APPLICATIONS

In the past two decades, radiofrequency (RF) technology is expanding dramatically,

since more and more electronic devices require an RF module to transfer data wirelessly. Therefore the demand for RF switches is increasing too. Currently, most RF switches are MEMS based devices, which have the disadvantages like high cost and energy consumptions. Lateral devices can be used as RF switches due to their low capacitance in HRS and ultra-low resistance in LRS. Comparing with MEMS switches, lateral PMC switches have the benefits like low cost and power consumption, so they are promising alternatives for MEMS switches. Figure I.7 is a schematic of a lateral PMC, of which the anode and cathode are parallel on top of the electrolyte. Compared to the vertical one, the spacing between the anode and cathode is usually larger (microscale), which gives the device a lower off-state capacitance. The resistance of LRS can be as low as 5 ohms, while the capacitance changes with the spacing between the anode and cathode. For a well packaged PMC switch, the insertion loss is very low, which is very important in RF switches [9]. Another application of lateral PMCs is the microfluidic valve, in which a microfluidic channel has a surface electrodeposit growth region fabricated at right angles to the fluid flow direction, as figure I.8 shows [10]. The fluid flows inside the channel when the filaments are absent, while when the filaments form between the anode and cathode, the hydrophobic filaments will stop the flow that turning the valve off.



Figure I.7: The schematic of a lateral PMC. When the switching voltage is applied across the anode and cathode, the metal ions will migrate to the cathode and reduce to form the filaments.



Figure I.8: The schematic of a lateral PMC based microfluidic valve.

Information security is attracting more and more attention, since more and more items needs a unique identifier to be labelled and tracked. Serial numbers barcodes and holographic tags are widely used [71]. However, they are not secure approaches which can be easily replicated to appear genuine. Secure approaches like covering the tags with fluorophores [72], coded nanostructures [73-75], and even custom DNA [76] are studied, which can provide extra layers of security but none of them are essentially random. Once the attackers discover the rules of the key generation, they can be replicated as well. Also smart cards are widely used on IDs and credit cards, which provide relatively strong information security but they are still vulnerable to power analysis attacks [77]. The ideal secure approach for labeling should be the physical unclonable functions (PUFs) [78], which can not only provide unique keys for each item, but also very difficult to be replicated. The radial PMCs have the potential to be PUF applications. In this work, we

investigated the uniqueness, randomness and attack resistance of the secure keys generated by radial PMCs.

In a radial PMC, the electrical field is uniform when voltage is applied in the initial condition. Figure I.9 is a schematic of a radial PMC, in which the edges of the anode and cathode are concentric circles. This makes the initial drift force uniform so that the randomness of the hopping process and Brownian motion will determine the shapes of filaments. In addition, the interface area between the anode and SE is much larger than the one between the cathode and SE, so the ion supply during the filament growth is better in radial PMC. Also relatively large filaments can be obtained, so the morphologies of the filaments can be observed easily. With a proper encoding algorithm, these filaments can be converted into data strings, which have the potential to be used as strong PUFs, which we call "dendritic PUFs". Also, the radial structure is ideal for investigating the fractal properties of the dendritic filaments.



Figure I.9: The schematic of a radial PMC device.

Vertical devices are suitable for memory devices [19], which are digital devices, the HRS and LRS can represent logic "0" and "1". As long as the HRS and LRS are distinguishable and consistent, the device is able to perform its function well. Therefore, relatively large tolerances of HRS and LRS are allowed in CBRAMs which means the fractal properties of filaments are not critical, so the vertical devices are not discussed in this work.

CHALLENGES AND FUTURE OF PMCS

In memory applications, retention, operation speed, power consumption and scalability are the most important considerations. Compared to the flash memories, CBRAMs have advantages in all these aspects[7, 18, 20, 29], which shows a very promising future in lowpower, high-speed, nanoscale ICs. Nevertheless, there are still many challenges to be conquered. The most important one is the integration with ICs as most of the early stage CBRAMs are Ag-GeSe/S based devices, which are not foundry compatible. Nowadays, foundry compatible CBRAMs have been reported [17, 20], which makes it a more powerful competitor in the emerging memory industry.

In RF switch devices, compared with the widely used microelectromechanical systems (MEMS) devices, PMC switches have two major advantages [9]. The first one is the low power consumption as it is a non-volatile device in which power is not necessary for remaining in the ON or OFF state and both of the switching voltage and energy are low. Another advantage is the fabrication of PMC switches, which is much simpler than that of MEMS devices as fewer process steps and no sacrificial layers are required. However, the challenge for the current PMC RF switches is the low number of switching cycles, as it needs an ultra-low resistance at in the LRS to reduce the insertion loss, which requires a much thicker conducting filaments than the ones in vertical PMCs. The thicker filaments require more energy for the erase operation, which means more heat will be generated during the erase operation because of the Joule heating effect. As a result, some metal may remain following the erase and reduce the cycling. The improvement of heat dissipation can improve the cycling significantly, which will be discussed in the next chapter.

In PUF applications, it is still a very new field and most applications are based on the manufacturing variations of the resistive memory (RRAM) or static random-access memory (SRAM), which are facing the problems like small hamming distance, high cost and power consumption [36]. Helfmeier, et al. reported that they have successfully cloned

these circuit based PUFs [37]. Our dendritic PUF has the advantages of low power consumption, robustness and strong attack resistance. All our current work is still laboratory based and more effort needs to be spent to create a real practical PUF system. After all, with the increasing demand in security, more and more attention will be attracted to PUFs and the dendritic PUF will become a strong competitor due to its outstanding performance.

Chapter 2

PMC BASED IONIC SWITCH

INTRODUCTION

Radiofrequency (RF) technology is growing rapidly. With the development of the Internet of Things (IoT) and sensor technology, more and more applications require RF modules [38, 39]. Currently, most RF switches are MEMS based devices, which have a suspended metal membrane anchored near the electrodes and a pull down electrode as figure II.1 shows. The switch turns on by pulling down the membrane by a pull-down electrode to short the circuit in the RF transmission line and turns off by releasing the membrane to open the circuit. The movement of the metal membrane can be achieved by electrostatic, magnetostatic, or piezoelectric, among which the electrostatic switches have the highest reliability at 0.1-100GHz [40]. There are still many issues for MEMS RF switches as they require power to maintain the ON state and switch speed and lifetime are limited by the mechanical properties of the metal membrane. In addition, the fabrication process is complicated and this adds considerable cost [9].



Figure II.1: A schematic of the MEMS RF switch.

Lateral Programmable metallization cell (PMC) devices used as RF switches have been reported [9]. The formation and dissolution of the metal filaments are based on the redox reactions. In the Ag/GeSe solid electrolyte system, as used in the first PMC-based RF switches, the switching energy is as low as a few nJ, which is similar to MEMS switches, but unlike MEMS switches, no power is required to maintain the on state since the PMC is inherently non-volatile. Furthermore, the fabrication process of lateral PMC RF switch is much simpler than that of MEMS devices. Lateral PMC RF switches can be easily fabricated with semiconductor device fabrication process, which is only a few steps of lithography, metal deposition and lift-off process, while MEMS RF switches are fabricated with surface micromachining techniques and packaged in inert atmosphere with very low

humidity and this packaging cost is currently very high [40]. Due to these superiorities, lateral PMCs are promising alternatives for MEMS switches.

As metallic filaments are the key to PMC device operation, many research studies have been performed to explore the relationship between filament properties and device performance [13-15, 41]. The morphologies of the filaments have also been observed and simulated [16, 42, 43]. However, most of those experiments and simulations were based on vertical PMCs, in which the metal filaments are nanoscale and formed inside the solid electrolyte and the research focused on the electrical properties, like resistance, retention, switching curve, etc. In lateral PMCs, the filaments are microscale and formed on the surface of the device. The contact interfaces between the filaments and anodes determine the resistance in LRS. Thus the morphology of the filaments are significant, since it impacts the contacts, while research work on this aspect is still lacking. As mentioned in the last chapter, the filaments are dendritic patterns that the fractal properties are critical. In this chapter, two important fractal properties are discussed. One is the fractal dimension [21] (FD) and the other one is the area ratio of the in-channel filaments (AR).

FILAMENT PROPERTIES IMPACTING SWITCHING PERFORMANCE

As discussed in Chapter 1, FD is an index demonstrating the complexity of a fractal pattern: with a higher FD, the pattern is more complicated and denser. In lateral PMC switches, the spacing between anode and cathode is micro scale while the height of the filaments are usually below 100 nm that is negligible comparing to its lateral size. Therefore all the filaments in lateral PMCs were treated as 2D patterns, whose FDs are between 1 and 2.
Usually, the area of the switching channel is only a small part of the whole device in a lateral PMC device. As figure II.2 shows, the region of the solid electrolyte between the anode and cathode within the electrode width is called the switching channel (the region inside the dashed blue box). Therefore, the filaments can grow outside the switching channel that the filaments have the arc-like shapes and we call these filaments "Group A filaments" and call those filaments inside the switching channel "Group B filaments". The positons where filament starting may impact the device performances of including HRS, LRS, erase energy, etc. To investigate the relationship between filament positions and device performances, a new parameter called area ratio (AR) is introduced, whose definition is the ratio of the area of the Group B filaments to the area of all the filaments. More details about AR is discussed in the following sections.

In this chapter, both the box-counting FD and AR of the filaments in lateral PMCs were analyzed. To further understand the mechanism of the filament growth, a KMC model was developed, which could be used to predict the morphology and growth rate of the filaments.



Figure II.2: Classification of the filaments in lateral PMC devices. The filaments in the red box formed outside the switching channel are the Group A filaments and the ones in the green box are the Group B filaments.

DEVICE FABRICATION

Various lateral PMC switches were designed in order to analyze device performance and filament properties. Figure II.3 is a typical layout of a lateral PMC switch. Structures with different electrode width w and gap spacing s were designed to exploit the best performance and filament growth behavior. The w values were 10, 15, 20, 50 and 100 μ m and the s values were 10, 15, 20 and 50 μ m. All the structures were designed on the same set of masks so that they could be fabricated on the same substrate simultaneously.



Figure II.3: The layout of the lateral PMC switch. Combinations of different electrode width and gap spacing were design.

Both silicon and low loss alumina wafer were used as the substrates. The details of the fabrication process are as follows.

Step 1: Patterning the chalcogenide layer. AZ 4430 photoresist was selected for this step because of its high thickness that facilitated the lift-off process for the device layers. Hexamethyldisilazane (HMDS) was spin coated on the substrate at 4000 rpm for 30s as the resist adhesion layer and then the photoresist was spin coated at 2000 rpm for 30s followed by soft baking at 100°C for 150s. The thickness of the photoresist was about 4.5 μ m. The coated sample was aligned with the photo mask by OAI 808 aligner and exposed under UV light for 32s, whose power was about 10mJ/cm² s, as figure II.4 (a) shows. The exposed sample was developed in MIF 300 developer for 4 minutes. After developing, the sample was partially covered with photoresist as figure II.4 (b) shows.



Figure II.4 (a): Masked exposure to get the chalcogenide pattern.



Figure II.4 (b): The developed photoresist.

Step 2: Deposition of the Ge₃Se₇ chalcogenide and silver. Both layers were deposited with a Cressington 308R thermal evaporation system. The chamber pressure for deposition was $3*10^{-6}$ mbar and the operation voltage was 4V. The deposition current was 35A and 45A

for depositing Ge₃Se₇ and Ag respectively. 60nm chalcogenide film was first deposited followed by 20nm silver and both of the deposition rates were about 0.1nm/s. A tungsten wire coil was placed on top of chalcogenide source and contacted the walls of the crucible firmly. Therefore, the chalcogenide source could be uniformly heated.

Step 3: Photo-doping. After unloading the sample from the Cressington evaporator, it was illuminated under an i-line UV lamp with a power of 2.5mJ/s-cm² for 2 hours as the photodoping process [44]. All the silver diffused into the chalcogenide film with assist of the UV as figure II.4 (c) and (d) show.

Step 4: Lift-off of chalcogenide. The sample was immersed in acetone for several hours until all the chalcogenide film on the photoresist was lifted off. Ultrasonic was used to remove any residual materials. Figure II.4 (e) shows a scheme of the fabricated chalcogenide film.



Figure II.4 (c): Thermal deposition of the chalcogenide and silver followed by photodoping process.



Figure II.4 (d): All the silver diffused into the chalcogenide layer after photodoping.



Figure II.4 (e): The silver doped chalcogenide film after lift-off.

Step 5: Patterning the silver anodes. AZ 4330 photoresist was patterned on the sample with exactly the same recipe as step 1. Figure II.4 (f) shows the patterned photoresist.



Figure II.4 (f): The patterned photoresist for silver anode deposition.

Step 6: Deposition of silver anodes. 80 nm silver layer was deposited with the Cressington evaporator and the depositing condition was the same as step 2.

Step 7: Lift-off of silver anode. The sample was lifted-off in acetone and ultrasonic agitation was applied as silver film has good ductility requiring ultrasonic to remove all the residual material.



Figure II.4 (g): Silver anode after lift-off.

Step 8: Patterning the nickel cathodes. AZ 3312 photoresist was selected because it has shorter developing time than AZ 4330, while chalcogenide could be etched by MIF 300 developer [44]. HMDS was spin coated with the same recipe as step 1 and then AZ 3312

photoresist was spin coated at 2000 rpm for 30s and then soft baked for 60s at 100°C. The exposure was also operated with OAI 808 for 8s. Then the sample was developed for 45~60s. Figure II.4 (h) shows the patterned sample.



Figure II.4 (h): The patterned photoresist for nickel cathode deposition.

Step 9: Deposition of nickel cathodes. 80nm nickel was deposited with Lesker PVD 75 Ebeam evaporation system. The chamber pressure for deposition was $3*10^{-6}$ Torr and the operation power was about 10%. The deposition rate was about 0.08nm/s.

Step 10: Lift-off of nickel cathodes. The sample was lifted-off in acetone for 5 minutes.



Figure II.4 (i): The scheme of the sample after nickel lift-off.

Step 11: Patterning the gold contacts. AZ 4330 photoresist was selected for this step and the same recipe in step 1 was used.



Figure II.4 (j): The scheme of the patterned photoresist for gold contacts deposition.

Step 12: Deposition of nickel cathode. 50nm gold was deposited with an Edwards E306A thermal evaporation system. The chamber pressure for deposition was $3*10^{-6}$ Torr. The deposition rate was about 0.1nm/s.

Step 13: Lift-off of gold contacts. The sample was lifted-off in acetone for several hours.



Figure II.4 (k): The scheme of the sample after gold lift-off.

Step 14: Patterning the protection layer. As silver is very easily got oxidized when exposed to air. Therefore AZ 4330 photoresist was pattern on the sample covering the switching channel and the recipe was the same as step 1.



Figure II.4 (l): The scheme of the finished sample.

REDOX REACTIONS IN PMC

A lateral PMC device comprises an electrochemically active anode, like silver (Ag) or copper (Cu) and an inert cathode, like nickel (Ni) or platinum (Pt). Both of the anode and cathode are fabricated on the same thin layer of electrolyte, usually made of chalcogenide glass, in which the anode metal ions can dissolve and migrate freely. As figure I.7 shows, when a positive voltage is applied on the PMC devices across the anode and cathode, the anode metal begins to oxidize to ions and the chemical reaction is

$$M \rightarrow M^+ + e^-$$
 (2.1).

The metal ions dissolve into the chalcogenide and then drift towards the cathode due to the influence of the electric field, while the electrons are collected by the anode and transport to the cathode through the external circuit. Once the ions reached the cathode, they get reduced as the chemical reaction is

$$M^+ + e^- \rightarrow M$$
 (2.2).

The reduced metal atoms become immobile and accumulate at the reduction position. Similar as the electroplating, the filament formation has two stages: nucleation and growth. The nucleation happens in the beginning of filament formation, during which ions get reduced at the cathode and become immobile atoms. Such atoms will cover on the surface of the cathode and meanwhile, these atoms will aggregate to form clusters which are called nucleus. Essentially, the filament formation is a thermodynamic process, during which the Gibbs free energy change (ΔG) determines the reaction direction if no external driving force is applied, since the system always prefers a lower ΔG . The definition of ΔG is

$$\Delta \mathbf{G}(\mathbf{r}) = \frac{4\pi}{3} r^3 \Delta \mathbf{G}_V + 4\pi r^2 \gamma \qquad (2.3),$$

where r is the nuclei size, ΔG_V is the Gibbs free energy change for filament formation, which is a negative value and γ is the surface energy which is positive value. In the equation 2.3, the first term is the volume free energy and the second term is the interfacial energy, so ΔG is related to the nuclei radius. Figure II.5 shows the relationship between ΔG and r, in which ΔG goes through a maximum value before decreasing. The maximum ΔG (ΔG^*) is the nucleation barrier and r* is called the critical size. When r is smaller than r*, it requires external driving forces (like power supply) to nucleation, while when r is larger than r*, stable nucleus are formed and they can continue to growth into larger metal clusters, which are the filaments [69]. When more and more atoms are reduced at these filaments, they grow toward the anode and the device is turned ON when the filaments touch the anode.



Figure II.5: A diagram of the change of Gibbs free energy of metal ions upon formation of a nuclei of radius r [69].

As all the redox reaction here are reversible, to turn the device OFF, a reverse bias is needed. During the erase process, the filaments are heated up due to Joule heating and the high temperature accelerate the oxidation reaction 2.1 at the filaments and the ions get reduced at the anode, which breaks the conducting bridge and eliminates the filaments [9, 29]. The increase of temperature can be calculated by $T_e=T_m+V_e{}^2R_f R_{th}$, where T_e is the temperature of filament during the erase operation, T_m is the room temperature (300k), V_e is the erase voltage, R_f is the resistance of filaments and R_{th} is the thermal resistance of the

solid electrolyte [7]. The erase voltage for lateral PMC is 3V. For the very low resistance devices ($<10\Omega$), filament melting was observed under SEM as figure shows. Assuming that the filaments were heated to the melting point of silver (1234.8K), substituting all the data into the equation, we can obtain R_{th}=1040K/W. With this R_{th}, the temperature of filaments with different resistance were calculated and the results are shown in figure II.6. Essentially, a lateral PMC is a thermodynamic system, in which the active metal can be either in metallic state or ionic state and the state with a lower energy is always preferred without an external driving force. Figure II.7 shows the relationship of Gibbs free energy between the metallic and ionic phases, in which T_c is the critical temperature that both states have the same free energy. For bulk metal, T_c is the melting point, while in lateral PMCs, the filaments are usually much smaller, so T_c should be lower than the melting point. Lateral PMCs are non-volatile devices, which means the filaments are stable without a power supply, so T_c of lateral PMCs should be much higher than the room temperature T_m. At T_m , it needs to overcome a barrier of ΔG for the metallic filaments to turn into the ionic phase. Such barrier can be lowered to $\Delta G'$ when the temperature is increased to T_e (the filament temperature during the erase operation) [69]. Once the metal atoms in the filaments are oxidized into ions, they will diffuse into the SE and finally the filaments break. Therefore, the erase operation of PMC is a heat-assisted diffusion process during which the erase power heats up the filament lowering the metallic-ionic-phase-change barrier, so the metallic atoms are more easily to diffuse into the SE.



Figure II.6: Calculated data of filament temperature vs. filament resistance during the erase operation and the erase voltage was 3V.



Figure III.7: The relationship of the Gibbs free energy between the metallic and ionic phases.

PHYSICAL MODEL OF ION HOPPING TRANSITIONS IN PMC

In this project, the Ag (anode), Ni (cathode) and Ge₃Se₇ (SE) system was selected due to the high Ag solubility and diffusivity [44]. The reason using Ag as anode is because it is more noble than Cu, so it will not react with the oxygen in the air easily improving the aging effect of the switch. The reason using Ni as cathode is because it is cheap and electrochemically inert. For germanium selenide, we used the compound with weight ratio of 30/70, since the selenium rich compound can provide high ion mobility but the composition may be instable during the fabrication if the selenium ratio is too high, so this 30/70 ratio is a good balance for ion mobility and composition stability. As mentioned above, the mechanism of the PMC devices is simply based on the formation and annihilation of metal filaments but the transport of the metal ions is complicated, involving both drift and diffusion due to the external electric field and diffusion down the chemical gradient. Furthermore, Brownian motion impacts the filament growth as it adds more randomness [41, 45-47].

The drift ion flux via hopping is

$$J_{dr} = \frac{-2k_BT}{q\Delta x}\sigma\sinh(\Delta\xi/2) \qquad (2.3),$$

where k_B is Boltzmann's constant, T is the temperature, q is the elementary charge, Δx is the average hopping distance, σ is the conductivity of silver doped chalcogenide film and $\Delta \xi$ is the driving force [32]. The driving force is due to the applied voltage, so it is expressed as

$$\Delta \xi = \frac{q \, V}{k_B T} \frac{\Delta x}{l} \tag{2.4},$$

where V is the applied voltage and l is distance between anode and cathode[48]. Also, V/l is the electric field E. Substituting equation 2.4 into equation 2.3, the drift flux can be expressed as

$$J_{dr} = \frac{-2k_BT}{q\Delta x}\sigma \sinh(\frac{q E}{k_BT}\frac{\Delta x}{2})$$
(2.5).

The electric field distribution in the device before the formation of filaments was simulated with COMSOL Multiphysics and figure II.8 shows that the electric field is uniform inside the switching channel and it is slightly higher at the corners of the electrodes.



Figure II.8: Electric field in the lateral PMC devices, when 3V bias was applied across the anode and cathode and the strongest electric field occurred at the electrodes corners. Simulated by COMSOL Multiphysics.

The diffusion is also a hopping transition caused by the chemical gradient of the metal ions. For the initial state of a lateral PMC, the chemical gradient is negligible as the chalcogenide film is pre-doped with silver and the doping is close to the saturation condition. The pre-dope is performed by depositing a thin layer of silver on top of the chalcogenide film followed by illuminating under UV light, so the silver is uniformly doped into the chalcogenide glass and the silver from the anode cannot enter the chalcogenide glass since the silver concentration is saturate. Therefore the initial distribution of silver in the chalcogenide glass is uniform. With the formation of the metal filaments, most of metal ions near the cathode and filaments attached to the cathode are consumed reducing the silver concentration in the SE [9, 15, 28], while there is a delay for the anode supplying the ions into the electrolyte, s that the chemical gradient is created. According to Fick's law, the diffusion flux of metal ions is

$$J = -D\nabla n \tag{2.6}$$

where J is the flux of metal ions, D is the diffusion coefficient of metal in chalcogenide and ∇n is the chemical gradient of metal ions.

The chalcogenide films used in PMCs are amorphous, so the distribution of the hopping sites is random which makes the silver ions hopping routes random. Therefore the exact position where an ion reaches the cathode (or the filaments attached to the cathode once they form) is random. In a real device, those randomly migrating ions finally formed dendritic filaments. Besides, in the solid electrolyte as a dynamic system, Brownian motion plays an important role in the particle movement [49, 50], since it introduce extra random movements into the filament formation [51-53], which can be described by a well-established theory called "random walk" [25, 50, 54]. Since Ge₃Se₇ is amorphous, in which the lattice confinement of the Ag ions can be ignored [55] and the area of the Ge₃Se₇ film can be regarded as infinite for the Ag ion movement. Therefore, the unrestricted random walk model can be used to describe the Brownian motion in PMC. Mathematically, the positions of the Ag ions at a certain point in time can be described as,

$$U(I, y) = \sum_{n=0}^{\infty} y^n p_n(I)$$
(2.7)

where U(I, y) is the matrix of positions of the particles, y^n is a coefficient in the expansion of U(I, y) representing the probability of a particle making a random walk to site I after n steps [56]. Figure II.9 is an example of Brownian motion of a particle at site A at time t1. In a uniform and isotropic material, the same probability y exists for the particle to move to any site nearby. If n steps are required for a particle moving from Site A to Site B, the probability for a particle moving from Site A to Site B is y^n . Equation 2.7 is the set of all the ion movements due to Brownian motion in the solid electrolyte.



Figure II.9: A schematic of Brownian motion.

Based on these three basic mechanisms of particles movement, numerous different filament patterns can be formed. A kinetic Monte Carlo (KMC) model based on these equations was developed as part of this work and used to simulate filament patterns under different conditions. Both the experimental and simulated patterns are all dendritic due to the random hopping routes and Brownian motion and there are some common features which will be discussed in the following sections.

ELECTRICAL PERFORMANCE OF LATERAL PMC SWITCHES

After these 14 steps, the devices were complete and ready for testing. Figure II.10 shows the image of the device, in which the gold contacts are slightly larger than the silver anode in order to secure the contact between the anode and filaments. It consumes a large amount of silver to form filaments, so the silver concentration in the chalcogenide glass is no longer saturation after the formation. Therefore the silver in the anode will diffuse into the chalcogenide. When a considerable amount of silver is dissolved, the anode will be discontinuous adding extra series resistance to the switch which can be eliminated by the larger gold contact. The test equipment was a semiconductor parameter analyzer (Agilent 4155C) with a probe station. All the devices were swept between -1 and 1V with a current compliance of 1mA. The sweep step was 0.01V/step and sweep speed was medium. Figure II.11 shows the switching curve of a lateral PMC switch: it starts from point O (-1V) and the device remains in HRS until Point A (~0.2V); the current increases dramatically after Point A and reaches the compliance at Point B (0.4V) where the filaments form and the device switches to LRS; then the voltage sweeps back through Point C and D and the filaments break and the device switches back to HRS at Point E.



Figure II.10: Image of fabricated device: (a) the view of the entire device; (b) the zoomed-in view of the switching area.



Figure II.11: The switching curve of a lateral PMC switch.

Five voltage sweeps were performed on a single device and the HRS and LRS data was plotted as figure II.12. The virgin state resistance is about 10M Ω that is marked as 'Ori'; most LRS values are around 100 Ω , except for the one after first programming; most HRS values are between 1~10M Ω , except for the one after the third erase that may be caused by incomplete erase operation. As an RF switch, the device must have a low on-state resistance (below 100 Ω). The contact resistance of the testing equipment was measure as 8 Ω and the theoretical resistance of the silver filaments are very low, since the filaments are microscale. Assuming the filaments are cylindrical with uniform radius, the resistance of a filament can be calculated by R= ρ I/S, where ρ is the resistivity and is 1.6*10⁻⁸ Ω for silver. For a 20 µm gap device, like the one shows in figure II.11, 1 is about 20 µm and the diameter of the filament is about 1 µm. Substituting all these parameters into the resistance equation, the resistance of one silver filament in the 20µm device is around 1.6 Ω . Therefore, the relatively high on-state resistances are most likely caused by the contact resistance between the anode and filaments.



Figure II.32: HRS and LRS of a lateral PMC switch.

Scanning electron microscope (SEM) was used to observe the contact area between the filaments and anode. Figure II.13 (a) is the SEM image of one of the tested device, in which the filaments are as marked by the red ovals. A closer look of the filaments in figure II.13 (b) and (c) shows that the contacts between the anode and filaments are not solid. Furthermore, the image of another device shows the evidence of the filament melting during the programming, since it would generate considerable heat due to the Joule heating effect. For example, when a filament tip touches the anode, the device resistance will be lowered significantly leading to a relatively high current. If the filament tip is small, it will results Joule heating in a very small volume that the local temperature at the filament tip will increase dramatically, which may melt and even evaporate some silver in the filaments leading to a relatively high on-state resistance.





Figure II.13: The SEM image of the PMC switch after programming. (a) Overview of a tested device in which two silver filaments were formed and connecting the anode and cathode; (b) zoomed-in view of the upper filament in image (a); (c) zoomed-in view of the lower filament in image (a); (d) image of the contact region where the Joule heat effect occurred and melted the filament.

In order to reduce the Joule heating effect and to improve the contact between the filaments and the anode, 700nm aluminum was deposited with the Lesker PVD 75 Ebeam evaporation system as figure II.14 shows. It will not only make the anode a better contact electrode on chalcogenide film, but also improve the heat dissipation during the programming. As mentioned above, the silver anode may partially dissolve into the chalcogenide glass resulting a poor contact with the filament, while the gold contact covers all of the silver anode that the filament contact with the gold layer instead. Also the thick alumina layer performs as a good heatsink reducing the Joule heating effect. Figure II.15 shows the performance of a device with the 700nm aluminum layer that the LRS are all below 30Ω and the lowest one was only 8Ω .



Figure II.14: Schematic of the lateral PMC switch with thick alumina contact layer.



Figure II.154: HRS and LRS of a lateral PMC switch with aluminum contact. FRACTAL PROPERTIES OF FILAMENTS

As mentioned in last section, the growth of filaments has several random factors, like hopping routes and Brownian motion. In spite of such random factors, the approximate directions of drift and diffusion are determined by the electrical field and chemical gradient. Thus, the filament growth condition varies when different configurations of the input pulse are applied. Figure II.16 is an example of the input pulse configuration. Within one pulse period, during t1, the pulse signal is active, so drift driving force exists during t1 only, while diffusion and Brownian motion are present all the time. Here t1 is the pulse width (PW) and t2 is the pulse interval (PI). The ratio of diffusion and Brownian motion are almost fixed, while the ratio of drift and diffusion can be controlled by manipulating the duty cycle, t1/(t1+t2).



Figure II.16: Input pulse configuration for programming the switch.

According to this pulse programming configuration, the lateral PMC switches were also tested with a semiconductor parameter analyzer (Agilent 4155C). The programming voltage V0 was 3V with a current compliance of 10mA. The reason for using 3V instead of 1V is that PMC usually requires a forming process could help tune the virgin state device into better working condition [57]. As mentioned above, there is a nucleation barrier for filament formation which has to be overcome to form stable silver clusters. We call those clusters "Stage 1 filaments" and they function as seeds layers for filament growth. Acutally, forming process is to overcome this nucleation barrier and form some stable Stage 1 filaments. Here, only virgin state devices were used for observing the filaments. Figure II.17 is the IV curve of the electroforming process of the lateral PMC switch.



Figure II.17: A typical electroforming curve of the lateral PMC switch.

To adjust the weight of drift and diffusion, 16 input configurations with different pulse widths (PW) t1 and pulse intervals (PI) t2 were used. With a shorter PW and a longer PI, the device would have a longer diffusion time by increasing the weight of the diffusion component and vice versa. Table II.1 shows the details of all the configurations.

# of input pulse configuration	Pulse width t1 (s)	Pulse interval t2 (s)
1	0.1	1
2	0.1	3
3	0.1	5
4	0.1	10
5	0.2	1
6	0.2	3
7	0.2	5
8	0.2	10

9	0.3	1
10	0.3	3
11	0.3	5
12	0.3	10
13	0.5	1
14	0.5	3
15	0.5	5
16	0.5	10

Table II.1: List of all the input pulse configuration used for programming the lateral PMC switches.

Once the filaments were formed, the images were captured under an optical microscope with a magnification of 1000X and figure II.18 shows an example of filaments formed. Essentially, the formation of the filaments is a process of crystallization, which contains two major stages, nucleation and crystal growth [58, 59]. These two stages were observed in these lateral PMC devices. Several small dense filaments were formed in the beginning of the programming corresponding to the nucleation and some early crystal growth stage. In this stage, the electric field is still relatively uniform. The growth at this point is classified as the Stage 1 filaments. A few of those Stage 1 filaments grow longer than others suggesting that they have larger electric field near their tips which can attract the Ag ions nearby leading to a fast growth. These "lucky" filaments finally reach the anode and those parts are classified as the Stage 2 filaments. Both the Stage 1 and 2 filaments are marked in figure II.18. Once the filaments were formed under all the 16 conditions, the FDs of both the Stage 1 and Stage 2 filaments were analyzed separately with ImageJ (Fraclac plugin, Box-counting fractal dimension, default setting) [70], and the results are showed in figure II.19. According to the results, the FDs of the Stage 1 filaments $(1.35 \sim 1.45)$ are larger than those of the Stage 2 filaments $(1.18 \sim 1.32)$, which is due to the changing of the electric field during the filament growth. In the beginning, the electric field is relatively uniform in the channel as figure II.8 shows, so the probability of forming the filaments is similar along the edge of the cathode, while after growth initiation, some filaments get closer to the anode so the electric field increase at the tips of these filaments leading to a higher probability to attract Ag ions and grow larger. Moreover, this is an avalanche effect that when the filament grows larger, the electric field is higher.



Figure II.18: Image of dendritic filaments formed in a lateral PMC switch. The Stage 1 filaments are small fuzzy filaments formed near the cathode and the Stage 2 filaments are more linear and in larger size.





As mentioned above, to analyze the location of the filaments, we classified the filaments into two groups based on their starting point: Group A filaments have starting points at the cathode corners, while the rest of the filaments are all belong to the Group B, as figure II.2 shows. For all the 16 conditions, the ratio of the filaments from Group A and B were obtained by analyzing the area of the filaments with ImageJ. The ratio of the area of the group B filaments over the area of all the filaments was calculated. This ratio is called area ratio (AR) for simple, whose definition is

$$AR = \frac{A_B}{A_A + A_B} \tag{2.8},$$

where A_B is the area of group B filaments and A_A is the area of group A filaments.

Figure II.20 shows AR under all the 16 growth conditions and figure II.21 shows the images of the formed filaments. Evidently, the Group A filaments dominate in most samples, since ratios of group B filaments are below 50% in most samples, which is because of two reasons. The first one is the strong electric field at the corners of the cathodes as showed in figure II.8, where the Ag ions were most likely to accumulate, while another reason is the depletion of the Ag ions in the switching channels. Initially, there are plenty of silver ions inside the switching channel due to the photo-doping. For the device showed in figure II.21, the gap spacing is 20 µm and the electrode width is 50 µm, so the area of its switching channel is 1000 μ m². As the thickness of the silver doping layer is 20 nm, the total amount of silver inside the switching channel is about 20 μ m³ in volume. The filament formation will consume the silver inside the switching channel first due to the strong electric field and it will form some Stage 1 filaments first. Assuming that the Stage 1 filaments will cover all the cathode edge and its thickness is about 1 µm, 20 µm³ silver can only support 400 nm filament growth in length. To continue the growth, either the anode or the chalcogenide glass outside the switching channel needs to supply the silver ions. For silver supply from the anode, it needs to oxidize atoms to ions first which can be a bottleneck for the silver supply. If the anode supply rate is low, there will be a silver ion depletion region inside the switching channel as figure II. 22 (a) shows. Then silver outside the switching channel will be driven to the cathode. During moving to the cathode, an ion is highly likely to be captured by the arc-like electric field near the switching channel and

then move to the cathode corner along the direction of the arc-like electric field, as figure II.22 (b) to (d) show. Therefore, the cathode corners are the preferred positions of filament formation. On the other hand, such depletion effect will create a chemical gradient between the chalcogenide glass inside and outside the switching channel. Due to this gradient, the Ag ions outside the switching channel will diffuse to the cathode to compensate Ag depletion. For a pulse programming, during t1 the voltage is active, so it keeps consuming the silver ions causing the depletion while during t2, the diffusion effect will compensate the depletion, which is the material relaxation time. Back to the figure II.20, almost no Group B filaments were formed under the 0.5s-PW programming. It is because during the long pulse width, most Ag ions inside the switching channel were consumed and only the Ag ions outside the switching channel could contribute the filament formation. For the 0.1s and 0.2s-PW programming conditions, AR is randomly between 30% and 60%, which indicates the sufficient silver supply inside the switching channel. The 0.3s PW looks like a critical point for Ag depletion. With a longer material relaxation time, more Group B filaments could form, suggesting the Ag depletion inside the switching channel, but not as server as the 0.5s-PW programming conditions, so that the depletion could be effectively compensated during the material relaxation time. Thus, the AR can be controlled by the pulse configuration that a shorter PW with a longer PI leads to more Group B filaments and vice versa.

To verify the change of the Ag concentration, energy-dispersive X-ray spectroscopy (EDX) was performed on a device right after forming filaments. The EDX characterization was performed using a JEOL JXA-8530F Hyperprobe with a 15kV accelerating voltage. In figure II.23, as expected, the EDX results shows that the Ag concentration in the switch

channel is lower than that outside the channel. The Ag atomic ratio outside the switching channel is about 10%, while it is lower than 6% inside the switching channel. There is an increase in Ag concentration after 30 μ m inside the switching channel, which indicates the presence of filaments.

Furthermore, as figure II.22 shows, when the PWs are 0.5s, there are almost no group B filaments formed due to the two reasons mentioned above, while when the PWs are lower, there is a higher probability to form Group B filaments, especially with longer PIs. Nevertheless, when the PWs are small (shorter than 0.2s), the effect of random hopping process and Brownian motion become more significant and the positions of the filaments are more random.


Figure II.20: The ratio of group B filaments under different growth conditions.



Figure II.21: Filaments formed under all this 16 growth conditions.



Figure II.22: (a) When ion is depleted inside the switching channel, almost only the ions outside the switching channel will contribute to the filament growth; (b) when an ion moves close to the cathode, it gets captured by the electric field; (c) the ion moves along the electric field; (d) the ion reaches the cathode corner and gets reduced there.



Figure II.23: The SEM images of the switching channel in the lateral PMC device with some Ag dendrites (filaments) formed at the cathode. The EDS measurements were applied along these two magenta dash lines and the plots on the right show the results that the Ag concentration outside the switching channel was quite uniformed, while the concentration decreased near the anode inside the switching channel.

SIMULATION APPROACH

Based on the three mechanisms of Ag ions movements mentioned above, the process of filament formation was also simulated with a Kinetic Monte Carlo (KMC) method in Matlab. A 2D lateral device structure as figure II.24 shows is used in this simulation, which includes the anode, cathode and electrolyte. The programming process has three phases: the ionization reaction at the anode, the drift and diffusion in the electrolyte and reduction reaction at the cathode. The preset Ag ion concentration in the electrolyte is 25% volume ratio, which is an approximation of the experimental photo doping concentration. To simplify the model, the electrolyte is assumed as an ideal isotropic dielectric material and the Ag ions have the same drift mobility, diffusion coefficient and Brownian motion frequency in all orientations at any position and the reduction only happens at the cathode and filaments.



Figure II.24: Structure of lateral PMC switch used in the KMC model. At the start of the simulation, the preset Ag ions are reduced at the cathode forming the filaments and reducing the Ag concentration. Meanwhile, the Ag atoms in the anode get

oxidized and diffused into the electrolyte to compensate the consumption. Based on the Marcus theory[60], the Ag oxidation rate in this simulation is

$$R = A \, e^{\frac{-Ea}{kT}} \tag{2.9}$$

where A is a coefficient of electron transfer reaction; Ea is the activation energy of Ag, which we used 0.26 eV here, since the work function of Ag is 4.26 eV and the affinity of Ge is 4 eV; and kT equals 0.026 eV at room temperature.

For the movements of the Ag ions, the drift-diffusion flux and Brownian motion probability are defined by equation 2.5, 2.6 and 2.7 respectively. To simplify the simulation, the velocity is define as

$$v_{dr} = \mu E \tag{2.10},$$

where μ is the silver ion mobility in chalcogenide glass and its value is about 10⁻⁶ cm²/Vs. According to the Einstein relation,

$$D=kT\mu/q \tag{2.11},$$

thus, an approximate value for D is 10^{-8} cm²/s. The electric field is approximately calculated by the equation

$$E=U/d$$
 (2.12)

where U is the voltage and d is the distance between the anode and the tip of the filaments (in the initial condition, the tips of the filaments are at the cathode edge). Once an Ag ion is reduced, d will be updated to derive the new electric field. In addition, to

simplify the model, the reduction reaction efficiency is set to 1 as when the Ag ions touch the cathode or the filaments, they will get reduced.

Based on this approach, several relationships between the switching parameters and filaments properties were investigated. The first is the relationship between the FDs and the switching voltage. Figure II.25 shows the simulated filaments whose growth condition was set to 3V, 0.3s PW and 3s PW. The morphology of simulated Stage 1 filaments is very similar to that of real filaments (figure II.18), which are dense and small filaments covering the edge of the cathode. Also morphologies of both experimental and simulated Stage 2 filaments are similar, which are thin and linear-like filaments. For the filaments in figure II.25, the FD of Stage 1 filaments is 1.50 while the FD of Stage 2 filaments is 1.24. Back to the figure II.19, it shows for that the experimental filaments, FDs of Stage 1 filaments are between 1.35 and 1.5 and the FDs of Stage 2 filaments are between 1.15 and 1.3, so for both the experimental and simulated filaments, the FD of Stage 1 filaments is 0.2~0.3 higher than that of Stage 2 filaments. Therefore, the simulated results match the experimental results. Moreover, there is a series resistance in the lateral devices so that they cannot switch under 2V before the forming process is performed, while with a large voltage the filaments are easily destroyed due to Joule heating [61]. Nevertheless, the simulation can predict the filaments morphologies under a wide range of a switching voltage. Figure II.26 (a), (b) and (c) are the simulated filaments formed by the switching voltage of 0.25V, 1.5V and 5V. As the figures show, it tends to form more stage 1 filaments and more branches of stage 2 filaments when the voltage is small, while when the voltage is large, it tends to form a small number of straight filaments with bifurcations near the anode. The reason for this trend is because when the voltage is small, the electric field is

too small to drive the ions and the diffusion dominates during the migration which tends to form more uniform filaments (stage 1 filaments), while the electric field increases when the filaments get closer to the anode and beyond a critical point, the drift dominates and begins to form more of the stage 2 filaments. In addition, bifurcations of filaments can be observed in both experimental and simulated results, especially near the anode. Figure II.27 illustrates the mechanism of this phenomenon. The electric field at the tip of the filament is so high just before reaching the anode that it will attract the Ag ions within a large area and also the Ag supply is more sufficient near the anode, so Ag ions will drift to the tip of the filaments from a wide angle α . Ag ions coming from different regions will reach the filament at different positions leading to different growth directions. For example, Ag ions above and below the black dashed line may results two growth directions as the red arrows. Thus, the ions drifting from different orientation bifurcates the filament.



Figure II.25: Simulated filaments with the growth condition of 3V, 0.3s PW and 3s PI. Like the experimental filaments, it comprises Stage 1 and Stage 2 filaments as well.



Figure II.26: (a) Simulated filaments with the growth condition of 0.25V DC. (b) Simulated filaments with the growth condition of 1.5V DC. (c) Simulated filaments with the growth condition of 5V DC.



Figure II.27: Schematic of the bifurcation phenomenon of a filament. All the ions within an angel α will be driven to the tip of the filament under an electric field. The ions coming from different regions will reach the filament at different positions leading to different growth directions of filaments as the red arrows indicates, which results the bifurcation phenomenon.

The second relationship is the filaments positions and the pulse intervals. Figure II.28 (a) and (b) correspond to the pulse intervals of 1s and 10s with the same voltage (3V) and pulse width (0.3s). Figure II.28 (c) and (d) are the images of experimental filaments under

the sample conditions of (a) and (b) respectively. As a result, in both the simulation and experimental cases, with a longer PI, Group B filaments (inside the switching channel) can grow larger. Therefore, Ag ions depletion can be a limiting factor of the filaments formation.



Figure II.28: (a) Simulated filaments with the growth condition of 3V, 0.3s PW and 1s PI; (b) simulated filaments with the growth condition of 3V, 0.3s PW and 10s PI; (c) experimental filaments with the growth condition of 3V, 0.3s PW and 1s PI; (d) experimental filaments with the growth condition of 3V, 0.3s PW and 10s PI.

Beside the innovative relationships, this simulation can be also used to explore some common and useful relationships. One is the switching time versus the voltage. The algorithm for the switching time simulation is basically counting the steps of ion hoping. Assuming it takes time t_0 for an ion to hop for the average hopping distance, if it takes n step for an ion hoping to the cathode or formed filaments, the total hoping time for one ion is (n*t₀). Assuming that the ion flux is constant during the growth and there are number of m ions moving simultaneously, if the total number of N ions contribute to the filament formation, the switching time is $N*n*t_0/m$, where t_0 and m are constant, so the switching time t is proportional to N*n. The raw data of switching time obtained from the simulation is unitless, but it can be calibrated with the experimental data. The calibrated data is showed in figure II.29. The black discrete data points are the switching time under different voltage obtained from the simulation and the red curve is the fitting curve whose expression is

$$t_{switching} = 7.82 * e^{-\frac{V}{2}} + 0.17 \tag{7}$$

which is an inverse exponential relationship in which the switching time deceases when the voltage increases.

Another relationship is the compliance current versus the on-state resistance. The algorithm for the resistance simulation is basically counting the number of atoms in the filaments. As the simulation is 2D, the resistance of the filaments can be expressed as $R=\rho l/w$, where ρ is the resistivity of Ag, l is the length of a filament and w is the width of a filament. To calculate the resistance of a filament, the switching channel is divided into serval strips as figure II.30 shows. The width of filaments in each strip is counted as w1, w2... wn. Therefore, the filament resistance is $\rho l_0 \sum_{i=1}^{n} wn$, where l_0 is the length of the strip. Neglecting the contact resistance, this value can be treated as the on-state resistance. Similarly, this data needs calibration as well. Figure II.31 shows the calibrated data, which is a linear relationship in a log-log plot.



Figure II.29: The simulated switching time vs programming voltage.



Figure II.30: Schematic of filament diving in the on-state resistance simulation. The filaments are equally dived into n strips and the width of the filaments in each strip is counted.



Figure II.31: The experimental data and simulated results of the on-state resistance versus compliance current with the same switching voltage of 3V.

The morphologies of the filaments are significantly influenced by the growth conditions. The FDs of stage 1 filaments are always higher than those of the stage 2 ones and according to the simulation, the ratio of the stage 1 filaments decreases with the switching voltage and also the large switching voltage has higher probability to cause the bifurcations in filaments near the anode. On the other hand, the ions depletion can change the positions of the filaments that when the ions supply is sufficient, it tends to form more filaments inside the switching channel. Contrariwise, if ions depleted in the switching channel during the filaments formation, it tends to form filaments at the cathode corners only.

Comparing with the experimental results, the results simulated by our KMC model matched well. In the simulation, it shows the two stages of the filament formation, nucleation and growth. The FDs of both Stage 1 and 2 filaments well match the experimental results, that FDs of Stage 1 filaments is about 0.2 to 0.3 higher than that of Stage 2 filaments. The filament bifurcation effect and ion depletion effect are also successfully simulated. Thus, this model can be a powerful tool to predict the fractal morphologies of the filaments, switching speed and on-state resistance in lateral PMC devices and it can be used to predict the behavior of other materials as long as the material's parameters are provided. This KMC model is promising to be used as a guidance for the designing, testing and optimizing the lateral PMC devices.

Chapter 3

DENDRITE PHYSICAL UNCLONABLE FUNCTIONS

INTRODUCTION

Physical unclonable functions (PUF) are attracting more and more attention since a unique identifier can be generated for every item that needs to be labeled, while it is extremely difficult to copy. The ideal PUF should be able to provide a large amount of unique secure keys and all of the secure keys are not only robust, but also resistant to attacks (e.g., cloning the secure keys based on the information revealed during the reading operation). Currently, most PUFs are based on silicon devices taking the advantage of the manufacturing variations, for which the critical issue is that the variations are too small. Even some of these circuit based PUFs are actually proved as clonable [37]. The other types of PUFs like artificial fingerprints [62] are facing problems like not enough randomness and considerable fragility. In this work, we invented an innovative PUF based on dendritic metalized patterns that addresses all these three issues.

The PUF application we developed is an optical strong PUF, in which the origination of the randomness and the mechanism of the random dendrite growth was investigated and verified by experiment. Hundreds of dendrites grown simultaneously under the same conditions demonstrated such randomness. Moreover, a Monte Carlo model based on the physical mechanisms of electrodeposition was built to simulate the growth of the dendrite and this matched the experimental results well.

PATTERN RANDOMNESS

The dendritic patterns are formed with silver ions in chalcogenide solid electrolyte (Ge₃Se₇) by electrochemical self-assembly, whose mechanism is explained in previous chapters. The silver is pre-doped into the chalcogenide through photodoping [44] and most

silver atoms lose electrons when doped into the chalcogenide. The positive charged silver ions will drift under an external electric field from the anode to cathode during dendrite growth and the silver anode works as a diffusion source that keeps supplying silver ions to the electrolyte to compensate for the consumption of silver ions. This ion drift-diffusion process in chalcogenide glass has been well characterized [63]. Importantly, this driftdiffusion process is also a very critical factor of the randomness, since both the drift and diffusion of the silver ions happen via hopping motions, which are random walks when the time window is larger than $1/[2 \pi v(T)]$, where v is the characteristic frequency under temperature T[14, 31]. For room temperature, v(T) of Ge₃Se₇ is about 10^{12} s⁻¹[^{16]}, while it took serval hundred microseconds for a ion migrate from the anode to cathode, since the ion mobility is around 10^{-6} cm²V⁻¹s⁻¹, and the device size 100 µm and 400 µm, leading to a transit time that is much larger than the time window. Moreover, the chalcogenide layer prepared with thermal evaporation is amorphous and contains a large amount of defects that add extra randomness to the hopping routes.

The random distribution of the silver ions in chalcogenide glass and Brownian motions as pure random walks [50] are factors of the randomness. As each ion has a unique initial position and hopping route, it reaches the cathode at different positions and gets reduced and becomes immobile there. The accumulation of those reduction positions finally leads to dense dendritic patterns, which we call "Stage 1 dendrites". Those Stage 1 dendrites actually slightly change the electric field as the tips have slightly higher electric fields attracting ions nearby. As a result, these Stage 1 dendrites have higher probabilities to trap and reduce the ions than the other areas on the cathode and cause the Stage 1 dendrites to grow longer and faster, which means it enters the second phase of the dendrite growth. Those Stage 1 dendrites compete with each other as well. The shorter distance between the dendrite tip and the anode, the higher the electric field and so more ions can get trapped and join the growing electrodeposit. In this phase, the dendritic patterns are thinner and more 1D-like than the Stage 1 dendrites, so we call them "Stage 2 dendrites". The Stage 2 dendrites are fractal and appear broadly similar at all levels of magnification. Such self-similarity property leads to finer structures when the scale goes smaller and mathematically, the dendritic patterns are considered as infinite complex [25]. Although, for a real dendrite the complexity is limited by the physical constraint (atom size), it still contains sufficient amount of minutiae as an essential requirement for PUF application.

DEVICE STRUCTURES AND FABRICATION PROCESS

To verify the randomness theory, both experimental and simulation work were performed. In order to explore the randomness, arrays of the radial structure devices were fabricated as figure III.1 shows. All the nickel pillars are connected by the nickel cathode layer and the silver anode is a continuous film with holes surrounding the pillars so that the initial potential is the same for every device in the array when voltage is applied. The purpose of the isolation layer is to prevent the growth of vertical dendrites.



Figure III.1: Schematic of the radial PMC array.

The radial PMC array was fabricated on silicon wafers. The details of fabrication process are as follows:

Step 1: Deposition of nickel ground cathode. The deposition was operated with a Kurt J. Lesker PVD 75 thin film deposition system equipped for magnetic sputtering evaporation. The chamber pressure before deposition was $3*10^{-6}$ Torr and it was 4 mTorr after turning on the Argon flow. The operating power was about 200W. The deposition rates were about 0.1nm/s and the total thickness was 60nm.

Step 2: Deposition of SiO₂ isolation layer. The deposition was operated with an Oxford Plasmalab 100 plasma-enhanced chemical vapor deposition (PECVD) system. The chamber pressure during deposition was about 1200mTorr and the operation temperature was 350 °C. The operating power was about 20W and the deposition rate was about 70nm/min. The total thickness was 100nm.

Step 3: Annealing of the SiO₂ isolation layer. In order to improve the isolation property of the film, the sample was annealed in a tube furnace at 525° C for 5 minutes under ambient. Step 3: Deposition of SiO₂ isolation layer. 400nm SiO₂ was deposited on the sample with PECVD and the recipe is the same as step 2.



Figure III.2 (a): Schematic of the sample after depositing nickel ground cathode and isolation layer.

Step 4: Patterning the cathode pillars and contact. AZ 4430 photoresist was selected for this step because of its high thickness that facilitated the lift-off patterning process.

Hexamethyldisilazane (HMDS) was spin coated on the substrate at 4000 rpm for 30s as the adhesion layer and then the photoresist was spin coated at 2000 rpm for 30s followed by soft baking at 100°C for 150s. The thickness of the photoresist was about 4.5 µm. The coated sample was aligned with the photo mask by an OAI 808 aligner and exposed under UV light for 32s, whose power was about 10mJ/cm² s. The exposed sample was developed in MIF 300 developer for 4 minutes. After developing, the sample was partially covered with photoresist as figure III.2 shows.





Figure III.2 (b): Patterned photoresist for cathode pillar deposition. The upper figure is the side and the lower figure is the top view.

Step 5: Etching SiO₂ isolation layer. The patterned sample was immersed in buffered oxide

etch (BOE). The etching rate was about 0.1nm/s, so it took about 9 minute to etch all the

SiO₂.



Figure III.2 (c): Schematic of the sample after BOE etching.

Step 6: Deposition of cathode pillars. To ensure that the filaments would grow on the surface of the chalcogenide, the height of the pillars must be greater than the chalcogenide thickness, thus the minimum thickness of the pillars was 600nm. For an easier lift-off process, aluminum was selected as the pillar material, but aluminum could be etched by MIF 300, so a nickel layer was deposited on it as a protection layer. 700nm of aluminum was deposited with a Lesker PVD 75 Ebeam evaporation system. The chamber pressure for deposition was 3*10⁻⁶ Torr and the operation power was about 27%. The deposition rate was about 0.3nm/s. After depositing the aluminum, 50nm nickel was deposited in the same equipment without breaking the vacuum. The deposition rate was about 0.08nm/s.

Step 7: Lift-off of the cathode pillars and contact. The sample was immersed in acetone for several hours until all the photoresist was dissolved. Ultrasonic might be used to remove the residual.



Figure III.2 (c): Schematic of the sample after fabricating the cathode pillars.

Step 8: Patterning the chalcogenide layer. The same as step 4.

Step 9: Deposition of chalcogenide and silver doping layers. Both layers were deposited with the Cressington 308R thermal evaporation system. The chamber pressure for deposition was 3*10⁻⁶ mbar and the operation voltage was 4V. The deposition current was 35A and 45A for depositing Ge₃Se₇ and Ag respectively. 60nm chalcogenide film was first deposited followed by 20nm silver and both of the deposition rates were about 0.1nm/s.

Step 10: Photo-doping. After unloading the sample from the Cressington evaporator, it was illuminated under an i-line UV lamp with a power of 2.5mJ/s-cm² for 2 hours, during which all the silver diffused into the chalcogenide film.

Step 11: Lift-off of chalcogenide. The sample was immersed in acetone for several hours until all the chalcogenide film on the photoresist was lifted off. Ultrasonic might be used to remove the residual.



Figure III.2 (d): The schematic of the device after fabricating the chalcogenide layer.

Step 12: Patterning the silver anode. Same as step 4.

Step 13: Deposition of the silver anode. 80 nm silver layer was deposited with Cressington evaporator and the depositing condition was the same as step 9.

Step 14: Lift-off of the silver anode. The sample was lifted-off in acetone and ultrasonic agitation was applied to help remove all the residual.





Figure III.2 (e): Schematic of the fabricated device. Upper figure is the side view and lower figure is the top view.

EXPERIMENTAL RESULTS

After fabrication, the whole wafer contains three type of devices with different diameters of growth regions: Type A is 200 µm; Type B is 800 µm; Type C is 2400 µm. Figure III.3 shows the layouts of the three designs. For the convenience of the testing, the wafer was diced into 1cm by 1cm square dies with a dicing machine. Figure III.4 is a photo of a die, which is a Type B device. All the dies were ready for dendrite growth and the growth operations were performed with an Agilent 4255C semiconductor parameter analyzer.



Figure III.3: The layout of three radial PMC arrays with different diameters. (a) $200 \,\mu m$ diameter; (b) $800 \,\mu m$ diameter; (c) $2400 \,\mu m$ diameter.



Figure III.4: The photo of the die of the radial PMC array. The anode and cathode are the indicated spots.

Since all devices in an array are radially symmetric, all the positions along the cathode edge are identical, so a sampling test (constant applied voltage) was used to growth the filaments. In the first two batches, the annealing step was not performed and most devices were shorted (anode to cathode) which was caused by bad isolation, whereas the yield was enhanced to almost 100% when this annealing of the isolation layer was performed. For a well isolated device, the filaments grow simultaneously in all the radial regions when voltage is apply between the anode and cathode pads, as figure III.5 shows.



Figure III.5: Image of the radial PMC array that filaments were formed simultaneously.

As in our earlier lateral PMCs, there are three ion transportation mechanisms in radial PMCs: drift, diffusion and Brownian motion. The ratio of the drift and diffusion plus Brownian motion can be adjusted by changing the growth voltage. For example, the dendrites in figure III.6 (a) were grown under 2V, while the ones in (b) were grown under

1V. Obviously, their shapes are very different from each other that the (a) is more linear like while (b) is denser. Their FDs were 1.2049 and 1.4347 respectively.



Figure III.6: Filaments formed under different growth voltage. (a) 2V; (b) 1V.

Beside the growth voltage, the device size significantly impacts the dendrite morphology. Figure III.7 shows the dendrites in Type A and B devices. Both of their FDs are around 1.2 since both of them were grown under 2V. Nevertheless, they have two main differences. First of all, the contrast of the ones in Type B device is higher, which indicates that the dendrites in Type B device are bolder. It is because the growth region is larger in Type B device that more ions joined the growth process. Also, there are fewer trunks of dendrites in the Type B device, among which two trunks are the longest and the angle between them was about 180°. The locations of the dendrite trunks actually indicate the competition between them during the growth. Just as in the case of lateral PMC devices, the ion supply in radial PMCs is limited as well. Figure III.8 is a schematic of the growth process showing that silver ions become depleted after forming dendrites. To continue the growth, the anode must resupply the solid electrolyte that create a chemical gradient for diffusion. On the other hand, as the dendrite grows longer, the electric field at the tip of the dendrite is increasing, which keeps attracting ions nearby as figure III.8 shows. When the drift velocity is much faster than the diffusion, most ions transfer to the tips. For smaller size device, the ion transportation distance is shorter, so ions may reach cathode or smaller dendrites and get reduced before arriving the longest trunk.



Figure III.7: Dendrite formed in different type devices with the same growth voltage (2V): (a) Type A device (200 µm diameter); (b) Type B device (800 µm diameter).



Figure III.8: Schematic of the ion transportation during the growth.

All the images in figure III.6 and III.7 were acquired by bright field imaging that are the essentially 2D projections of the dendrites, while the dendrites are actually 3D structures. To reveal the 3D morphology, dark field imaging was used. Figure III.9 shows the light path of both the bright and dark field configurations [64]. In the bright field configuration, all the light reflected by the sample is collected by the objective, while in the dark field

configuration, only the light scattered by the sample can be collected by the objective. Therefore, only the rough surface where light gets scattered can be imaged.



Figure III.9: Light path of the microscope: (a) bright field; (b) dark field [64]. Figure III.10 shows the comparison between bright field and dark field images for all the three samples mentioned above. For simplicity, we named them sample 1, 2 and 3 from top to bottom. Sample 3 has the highest contrast in the dark field image indicating its rough surface is reflecting more photons than sample 1 and 2. Sample 1 has the highest brightness in bright field imaging and it even has the metal luster which is an evidence of a smooth surface and its lowest dark field imaging contrast also suggests this.



Figure III.10: Bright field (left) and dark field (right) image of the dendrites. Upper images are Type A device programmed with 1V; middle images are Type A device programmed with 2V; lower images are Type B device programmed with 2V.

Such morphology difference does not only exist between different devices, but even within a single device as the local dendrite morphology can vary. Figure III. 11 shows an example: in the bright field image, the dendrite becomes shinier when getting close to the anode; in the dark field image, the shinier part has lower contrast like the sample 1 in figure III.11. It reveals that the dendrite is smoother at the anode side.



Figure III.11: Bright field (upper) and dark field (lower) images of the Type 2 device dendrite. The morphology of the dendrite when getting close to the anode as marked in the green box.

To further verify the assumption of 3D morphologies, Atomic-force microscopy (AFM)

and optical profilometry were used to observe the dendrites. Figure III.12 shows the optical

profilometry results for dendrites in a Type B device, in which the dendrites' 3D morphology is clear, especially from the side view. Moreover, in figure III.12, an annular dendrite can be clearly observed around the cathode, which is a Stage 1 dendrite. According to figure III.13, the height of the dendrites is between 10 to 30 nm and it varies rapidly.

AFM scanning was also performed to characterize the dendrite surface. Unlike optical profilometry, the scanning area in the AFM is much smaller but it provides better resolution and accuracy. A sample with transition morphology was selected and the scanning area was on the transition region. Figure III.14 shows the AFM scanning results, the dendrite in the red oval has similar microscopic view to the ones in the green box of figure III.11. There two features for those dendrites; first one is that the average height of dendrites is higher and another is that the changing of the height is not rapid. In other words, the morphology of those rougher dendrites (outside the red oval) look like mountains, while the smoother ones (inside the red oval) look like mesas.


(a)



(b)

Figure III.12: Image of dendrites acquired by optical prolifilometer: (a) top view; (b) side view.



Figure III.13: Height measurement on a crossection of the dendrite.



Figure III.14: AFM results of the dendrites. The part in the red oval was the dendrite with metal luster and the AFM scanning shows a larger height of dendrites in the red oval. Because the growth process is random, even for dendrites which form simultaneously, they are all different from each other. To investigate the randomness of the dendrites in the same die, a sampling test was performed on Type B devices. There are 60 radial PMCs for dendrite growth on a single die. After growing all the dendrites simultaneously, 23 of them

were captured with bright field imaging and the microscope settings for the capture (magnification, brightness, contrast and ISO) were all the same. All the dendrites look similar but are indeed different from each other. Once all the sample dendrites were captured, the images were converted to binary images, since the Fraclac plugin of ImageJ required binary images to analyze the fractal dimension (FD) [70]. Box-counting method is provided by Fraclac. For a binary pattern (black background with white pattern), it uses small boxes to cover the pattern, just like the example of figure I.4 and uses equation I.2 to obtain FDs. The binary process was performed with Matlab image process toolbox. Threshold color filtering was applied first to clear everything except the dendrites and then binary process was applied. Figure III.15 shows a comparison of the original and processed images. As we can see, most details of dendrites are kept after the binary process, but it still loses some details especially the very fine structures at the tips. In order to reduce the influence of the binary process, same process parameters were used for all 23 images.



Figure III.15: (a) Bright field image of the dendrite; (b) binary image converted from (a) with Matlab image process toolbox that was ready for FD analysis.

After the binary process, FDs of dendrites were analyzed with FracLac in ImageJ and the results are in figure III.16. FDs randomly distribute between 1.28 and 1.49 and the average FD is 1.37. Sizes of dendrites were also measured, which is defined as the distance between the tip of the longest trunk and the center of cathode. The results are also in figure III.16. 40% of the dendrites are longer than $350 \,\mu\text{m}$ which is very close to the anode $(400 \,\mu\text{m})$, while the rest of them are between 200 and $350 \,\mu\text{m}$. As a result, even for the dendrites in the same die and formed simultaneously with exactly the same growth condition, the morphology of every dendrite is unique.



Figure III.16: Statistic results of FD and pattern size of the dendrites formed simultaneously.

PUF APPLICATION

From the thermodynamic aspect, the random hopping transportation of drift and diffusion plus Brownian motion supplies the entropy in the dendrite growth process creating the minutiae[65, 66]. Those minutiae lead to the cell-to-cell variation of radial PMCs, which is a key attribute to be employed in PUF applications, since random secure keys could be generated. Also the pool of the secure keys can be huge since the self-similarity property of dendrites endows the ability to contain nearly infinite information within a single radial PMC. Figure III.17 shows an example of the self-similarity in dendrites. Here we introduce a concept fractal generation (FG), which describes the order of bifurcation on dendrites. FG1 is the trunk of the dendrite directly connecting the cathode and FG 2 is the main branch of the dendrite after the first bifurcation. In other words, FG n is the part of dendrites after the (n-1)th bifurcation. If the scanning equipment is good enough, the final FG is atomic scale. To quantify the theoretical information units u_n is given by

$$u_n = N_1^n / N_1 = N_1^{n-1}$$
 (3.1),

where N_1 is the number of segments in FG1 which will be repeated in next FG. It is related to the initial scaling factor ε_1 by

$$N_1 = \varepsilon_1^{-D} \tag{3.2}$$

where D is the fractal dimension. Substituting equation 3.2 into 3.1, un can be expressed as

$$u_n = \varepsilon_1^{-D(n-1)} \tag{3.3}.$$

At the magnification of revealing FG n, the total information capacitance In is

$$I_n = B^{u_n} = B^{\varepsilon_1^{-D(n-1)}}$$
(3.4)

where B is number of information units at a single point, including the information of color, brightness, contrast, etc. If the information units are treated as binary information containing 2 states "0" and "1" representing the absence and presence of the dendrite at the target position as figure III.18 shows.



Figure III.17: Micrograph of a radial silver dendrite (top) illustrating fractal branching at decreasing scale (bottom images). The yellow dots are the branching points and the yellow arrows indicate the main branches.



Figure III.18: Scheme of the binary information of dendrites. The pattern is converted as a pixel matrix and the locations with the presence of dendrite are marked as "1" and the rests are marked as "0".

The relationship between max n and the image resolution R is

$$n_{max} = \log_{\varepsilon 1} R - \log_{\varepsilon 1} S \tag{3.5},$$

where S is the size of dendrites. For dendrites in Type B radial PMC, ε_1 is around $\frac{1}{2}$, FD is about 1.37 and the average size of Type B device dendrites is about 300 µm. Substituting these number into equation 3.4 and 3.5, the maximum fractal generation and information capacitance at a certain resolution can be obtained. Several typical resolution are selected and the results were listed in Table III.1. 10 µm is the resolution that can be reached by a cell phone camera with a 100X magnifier; 1 µm is the maximum resolution for optical microscopes; 100 and 10nm resolution images could be acquired by SEM; 0.16nm is size of silver atoms. Obviously, even for 10 µm resolution, the information capacitance is as high as 2^{44} and the theoretical maximum information capacitance is nearly infinite. Thus, the secure key pool should be large enough for most PUF applications.

Image resolution	Max n	un	In
10 µm (cell phones with 100X lens)	5	44	2^44
1 μm (maximum resolution of an optical microscope)	8	770	2^770
100 nm (SEM)	11	13307	2^13307
10 nm (SEM)	15	5.9E5	2^5.9E5
0.16 nm (size of a silver atom)	20	6.8E7	2^6.8E7

Table III.1: Information capacitance of radial PMC at different resolution when FD is 1.37 and ε_1 is $\frac{1}{2}$.

The ideal approach to extract minutiae of dendrites is to build an algorithm based on the analysis mentioned above. However, it will take a lot of time and effort to develop a sophisticated algorithm. Fortunately, there are some open source algorithms which can be used such as scale-invariant feature transform (SIFT) [67] and local binary patterns (LBP) [68]. SIFT can extract the local features in images and is widely used in computer vision. It is an ideal algorithm for pattern recognition. ImageJ has the feature extraction plugin that can perform SIFT process on dendrites images. Figure III.19 shows the features of dendrites extracted by ImageJ.



Figure III.19: Features on dendrites extracted by SIFT process with ImageJ. Theoretically, any 2D pattern can be replicated if the scanning and printing equipment is good enough, but this is not the weakness of the dendrite PUF, since the 3D morphology is extremely difficult to clone. One rule for PUFs is the verification process cannot reveal all the information contained in a secure key. When recording the PUF information into the database, optical profilometry or AFM scanning can be used to characterize the detailed information of the morphology. Once a relationship between the morphology and light scattering is built, the light scattering detection can be performed for authentication without unfolding the 3D morphology information. Chapter 4

ION HOPPING MODEL AND SIMULATION OF PMC DEVICES

ION HOPPING MODEL

According to the experimental data of both lateral and radial PMCs, we propose an ion hopping model to describe the ion behaviors during the filament growth in PMCs. As mentioned in Chapter I and II, both the drift and diffusion movements in solid electrolyte (SE) are hopping processes and the drift and diffusion ion fluxes are described by equations 2.5 and 2.6 respectively. During growth Stage 1, the electric field is uniform and ions are uniformly and heavily doped in the chalcogenide glass electrolyte. The random hopping process and Brownian motion lead to the random fractal filaments with relatively high fractal dimensions. After forming some filaments, growth enters the Stage 2 phase as the tips of filaments have higher electric field than the cathode as they are closer to the anode. Such filaments have higher probability to capture ions. Moreover, the drift movements and filament formation can deplete the ions in the SE, while the diffusion movements during the relaxation time when growth voltage is inactive will compensate the depletion. Under a severe depletion condition, very few ions are present near the filaments. To continue the growth, ions are driven from the locations far away from the filaments by the electric field. With a longer drift distance, an ion has a higher probability to be captured by the tips. Therefore, only a few filaments can continue the growth and form low fractal dimension filaments.

When a relatively long relaxation time is given, the pulse interval described in Chapter II, the ions have a long time to diffuse to the depleted area and this significantly reduced the drift distance and leads to filaments with relatively high fractal dimension.

Similarly, the growth voltage has the same impact on the fractal dimension. A higher voltage creates a higher drift flux that leads to lower-fractal dimension filaments, while a lower growth voltage results in higher-fractal dimension filaments. With a higher growth voltage, the ion drift velocity is higher, so most ions are driven to the tips of the long branches, as figure III.8 shows. Like in lateral PMCs, the ion depletion happens in the chalcogenide glass, but there is no outside switching channel region supplying ions in radial PMCs. All Ag ions are supplied by the anode after depleting the pre-doped Ag ions. As the ion drift velocity is much higher than the diffusion velocity under a relatively high voltage, Ag ions are driven to the tips of filaments straightly leading to linear-like filaments with relatively low FDs. If the growth voltage is lower, the drift velocity is lower, so the diffusion movement and Brownian motion play more important roles and the routes for ions moving to filament tips are less straight. Moreover, the depletion effect is less server in the lower-voltage conditions, so the moving distances for Ag ions are shorter. If the initial positon of an Ag ion is too close to an existing filament, the ion has a high chance to touch the body of the filament and get reduced there before reaching the filament tip as figure IV.1 shows. Therefore, with a lower growth voltage, it tenders to form more branches on the filaments leading to a higher FD.



Figure IV.1: Schematic of an Ag ion moving to the filament under a relatively low voltage. The ion is reduced before reaching the filament tip.

ALGORITHM

To better understand the mechanism of dendrite growth, a kinetic Monte Carlo (KMC) model based on the ion hopping model was built to simulate the ion transportation and redox reactions in radial PMC devices. Essentially, the mechanism of dendrite growth in radial PMC is the same as the programming of a lateral PMC, so there are also three parts of ion transportation: drift, diffusion and Brownian motion. Both the drift and diffusion migration are via ion hopping, whose mechanism is described in Chapter II. The first radial PMC model is based on the algorithm of the lateral PMC. Figure IV.2 shows a scheme of the matrix representing a radial PMC. First of all, a matrix is created with the center area marked as cathode, the area outside the dashed circle marked as anode and the rest marked as chalcogenide. The red dots in the chalcogenide area represent the pre-doped silver ions which supply the dendrite growth in the beginning.

When voltage is applied, the ions begin to move towards the cathode. For the initial condition, no dendrites are present, so the electric field is uniformly pointing from anode to cathode, which drives the ions to the cathode. For convenience, a polar coordinate system is built inside the matrix as figure IV.3 shows. The black pixel in the center of the matrix is the cathode and the red pixel is the silver ion. The position of the ion is described by angle α and distance d. For the drift movement, the ion moves towards the cathode without changing α too much. Once the ion reaches the cathode it reduces to an immobile atom and accumulates there to form dendrites. With the process of the growth, the dendrites become larger and larger consuming silver ions nearby leading to a silver depletion region.



Figure IV.2: The schematic of matrix in KMC model representing a radial PMC.



Figure IV.3: The polar coordinate system in the matrix.

A snapshot of simulation halfway through the growth process is shown in figure IV.4, in which trunks of dendrites were formed and caused a silver depletion region to form inside the dashed circle. Due to the presence of the chemical gradient, diffusion occurs and its direction is pointing to the center. On the other hand, the electric field is not uniform anymore. For example, in figure IV.5, some dendrites are formed and the transportation of the silver ions are driven by both the diffusion and drift. As the electric field changes, the ion tends to drift to the tip of the dendrites due to the high electric field there.



Figure IV.4: The formation of dendrites consumes silver ions in chalcogenide and leads to a silver depletion region as marked by the dashed circle.



Figure IV.5: Schematic of the drift and diffusion orientation after forming trunks of dendrites.

Brownian motion (BM) plays an important role since it adds more randomness to dendrites. The algorithm for BM is a random walk to any adjoining pixels of the ion position. Figure IV.6 illustrates the BM in the model. If a silver ion is at the red pixel, it has a probability y to randomly move to any of the yellow pixels during the drift and diffusion. This probability y is an adjustable parameter that could be calibrated by experiments.



Figure IV.6: Schematic of the Brownian motion in the model. The red pixel is the position of the silver ion, which has a probability y to move to any of the yellow pixels.

The ion reduction is another important part during dendrite growth. In the simulation, it is achieved by a reduction judgement. As figure IV.7 shows, when a silver ion moves to a pixel where is adjacent to the dendrites, it will get reduced and frozen there. Such

judgement is performed after every moving step including drift, diffusion and BM, as long as the electric field is applied.



Figure IV.7: Schematic of the reduction judgement in the model. When the ion move to a pixel next to the dendrites, it gets reduced.

Based on the algorithm mentioned above, simulation results were obtained. Figure IV.8 shows two simulated patterns, in which (a) is simulated with low voltage and (b) is with high voltage. According to the results, the dendrites are fractal and random. Both Stage 1 and 2 dendrites match the experimental results well but the pattern still looks artificial since it roughly forms a cross shape. The reason is that the polar coordinate system in our matrix is not perfect and α changes slightly during the migration to cathode. However, if α equals 0, $\pi/2$, π and $3\pi/2$, it does not change during the migration, so the dendrites tend to grow along these four direction leading to the cross shape.



Figure IV.8: Simulation results with different voltage: (a) low voltage; (b) high voltage. HOPPING ALGORITHM

In order to eliminate the artificial component of the drift, a hopping approach was introduced. Figure IV.9 illustrates the hopping process. When an ion is at the red pixel, it has a distance of d and angle of α from the cathode. The hopping sites are randomly distributed in the solid electrolyte (SE) region where ions can hop to. Under the driving force of the electric field, the ion's hopping direction is restricted, which is angle β from the line of the ion and cathode, so the ion can only transit to the yellow pixels, but the exact hopping site is undetermined. This angle β is called the wiggle angle here and it increases when the electric field decreases. Such a hopping approach makes the simulation closer to the real mechanism and the results look more natural. Figure IV.10 shows 4 dendrites generated by the simulator with exactly the same parameters, but they look all different from each other just like the real dendrites in radial PMCs.



Figure IV.9: Hopping approach in the KMC model. The red pixel could randomly move to any of the hopping site (yellow pixels) within a wiggle angle β .



Figure IV.10: Simulated dendrites with same parameters.

Similar as the previous model, the electric field also plays an important role in the hopping model that high and low electric fields can generate totally different patterns. As figure IV.11 shows, the left image is the dendrite generated with low electric field which has higher FD and area than the dendrite generated with high electric field.



Figure IV.11: Dendrite patterns generated by the simulator with low (left) and high (right) electric field.

APPLICATION OF THE SIMULATION

The simulation algorithm is based on the ion hopping model with drift, diffusion and BM. Thus, the matching of the experimental and simulation results proves the validity of the ion hopping model in PMC. With the help of the simulator, we can not only understand the mechanism of ion transportation better, but also predict the morphology of the dendrites in real PMCs. Also, it can simulate some extreme conditions which cannot be easily performed by experiments. For example, figure IV. 12 shows the simulated dendrite patterns under different anode supplying rate. In figure IV.12 (a), the anode supply rate was set to a high value that ions never get depleted in the SE, so there are ions everywhere

and the ion moving distances are very short leading to a very dense pattern. In case (b) and (c), the anode supply rate was set to a medium and low value respectively, so the ion moving distances are longer than those in case (a) leading to thinner patterns.



Figure IV.12: Simulated dendrite patterns with different anode supply: (a) high anode supply; (b) medium anode supply; (c) low anode supply.

Furthermore as the simulator can generate complicated dendrites, such dendrites can be used as low-cost weak PUF applications. As a 2D pattern, it can be replicated with highresolution scanning and printing equipment, but the cloning process is costly. Therefore, the weak PUF application can be used for labelling low-value items that the cloning cost is even higher than the item value.

RELATIONSHIP BETWEEN GROWTH CONDITONS AND FRACTAL

DIMENSIONS

Both the experimental data and simulation results prove that the fractal dimension of a filament in PMC is strongly related with the growth conditions. With a relatively long pulse width, the ion depletion effect is critical that ions need to transport for a relatively long distance to form filament. The chance for an ion to be captured by the longest filaments increases with the ion transition distance. Thus, it tenders to form more liner-like and

lower-FD filaments, when the pulse width is longer. On the other hand, the larger growth voltage leads to a higher drift ion flux which also depletes the ions faster, so the higher growth voltage will also cause lower-FD filaments. Table V.1 shows the relationship between the growth condition and fractal dimension according to experimental and simulation results.

Growth conditions	Low FD condition & examples	High FD condition & examples		
Pulse width (PW)	Long PW: 0.3s, FD=1.29	Short PW: 1ms, FD=1.44		
Pulse width (PW)	Long PW, FD=1.16	Short PW, FD=1.23		
Simulated results				
Growth Voltage (V)	High V: 3V, FD=1.34	Low V=0.3V, FD=1.70		
Growth Voltage (V) Simulation results	High V=5V, FD=1.13	Low V=0.4V, FD=1.62		

Growth Voltage (V)	High V: 2V, FD=1.31	Low V: 1V, FD=1.50
Growth Voltage (V) Simulation results	High V, FD=1.50	Low V, FD=1.57

Table V.1: Relationship between filaments' growth conditions and fractal dimensions with examples.

CONCLUSION

Lateral PMC can be used as an RF switch which is a currently a rapidly expanding area, since more and more commercial electronic devices require an RF module to obtain Internet access. The fractal property of the dendritic filaments in lateral PMC impacts its performance significantly since the morphology of the dendrites influence the lowresistance state (LRS) resistance. Fractal dimension (FD) and area ratio (AR) of Group B filaments (formed inside the switching channel) are introduced to analyze the fractal properties of the dendrites, which vary with the growth conditions. The growth of dendrites can be divided into two stages: Stage 1 is the nucleation and early growth of the dendrite while the electric field is relatively uniform; Stage 2 is the major dendrite growth in which ions are captured by several main branches. The Stage 1 dendrites have higher FDs and cover all the cathode while Stage 2 dendrites are more linear-like and finally connect the anode and cathode. The ratio of Stage 1 dendrites increases with decreasing electric field. AR is related to the ratio of drift and diffusion. When a pulse voltage is active, ions can be reduced at the cathode or formed filaments and ion depletion effect in the solid electrolyte (SE) inside the switching channel may happen when the anode supply rate is lower than the ion consumption rate. Once the inside-channel SE is ion depleted, it has to drain the ions outside the switching channel to form Group A filaments. With a longer pulse interval (PI), the SE has a longer material relaxation time when ions outside the switching channel can diffuse inside to the switching channel to compensate for the depletion, so it has a higher probability to form Group B filament and AR is higher.

An ion hopping model with drift, diffusion and Brownian motion (BM) has been proposed to explain the relationship between the growth condition and fractal properties and verified by experimental data. The KMC simulation based on the ion hopping model has been developed and the simulation results match the experimental results well, predicting the dendrite morphology. Beside the silver-chalcogenide system, this KMC model can be used to predict the performance of the other materials as long as the materials' parameters are provided.

The growth of the dendrites is a random process which leads to unique dendrite patterns for every instance of growth. Even when the growth conditions are exactly the same, the dendrite patterns are different from each other due to the random hopping transportation and BM. An array of radial PMCs was fabricated and tested and the results meet such expectations. All the dendrites formed on the same die simultaneously are unique. Because of the self-similarity, the information capacitance of dendrites is extremely large. In addition, the 3D morphology of dendrites has unique light scattering, which makes the dendrites exceedingly difficult to replicate. Physical unclonable functions (PUFs) is still very new area but those features of dendrites make radial PMC a powerful candidate for strong PUF applications.

A KMC model based on the ion hopping model was also developed to verify the randomness theory of dendrites and predict the filament morphologies under different growth conditions. Also, the dendritic patterns generated by the KMC model can be used in weak PUF applications for low-value item labeling.

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