Electroplating of Aluminium on Silicon in an Ionic Liquid

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Abstract

Electroplating of aluminium (Al) on silicon (Si) substrates has been demonstrated in an above-room-temperature ionic liquid for the metallization of wafer-Si solar cells. The electrolyte was prepared by mixing anhydrous aluminium chloride and 1-ethyl-3-methylimidazolium tetrachloroaluminate. The plating was carried out by means of galvanostatic electrolysis. The structural and compositional properties of the Al deposits were characterized, and the sheet resistance of the deposits revealed the effects of pre-bake conditions, deposition temperature, and post-deposition annealing conditions. It was found that dense, adherent Al deposits with resistivity in the high $10^{-6} \Omega\text{-cm}$ range can be reproducibly obtained directly on Si substrates.

1. Introduction

Room-temperature or near-room-temperature electroplating of aluminium (Al) requires a nonaqueous solvent for an Al precursor. Many solvents have been reported for this purpose [1], including organic solvents and ionic liquids. Three types of organic solvents have been used to dissolve Al halides for Al electroplating: aromatic hydrocarbons [2], dimethylsulfone [3], and ethers [4]. Although high quality Al deposits can be obtained with these solvents, the relatively narrow electrochemical window, low electrical conductivity, low solubility of Al halides, high volatility and flammability make industrial applications of these organic solvents limited. Ionic liquids are a relatively new class of solvents for Al electroplating. They are characterized by high electrical conductivity, low viscosity, low toxicity, non-flammability, high thermal and chemical stability, and wide electrochemical window, making them ideal solvents for Al electroplating. Various ionic liquids for Al electroplating have been reported [5-15], which are typically mixtures of aluminium chloride (AlCl_3) and an organic halide (RX), such as 1-ethyl-3-methylimidazolium chloride (EMIC) and 1-butyl-3-methylimidazolium chloride (BMIC). These ionic liquids show adjustable Lewis acid-base properties, which are acidic when the molar ratio of AlCl_3 : RX is >1 . Al electroplating can be performed only under acidic conditions.

Electroplating of Al in an ionic liquid has been carried out on metallic substrates such as stainless steel [12], platinum [6, 10], tungsten [6, 7, 11], gold [9], copper [8], iron [10], and glassy carbon [6]. The deposited Al often serves as an anticorrosion coating. Although Al electroplating on silicon (Si) has been reported [15], report of electroplated Al on Si substrates as a low-cost metallization method in Si photovoltaics [16] and microelectronics has yet to appear in the literature. A major difference between electroplating on Si substrate vs. on metallic substrate is the high resistivity of Si, which is typically in 10^{-2} – 10 Ω -cm. For most metals, the

resistivity is in 10^{-5} – 10^{-6} Ω -cm. Another problem is the native oxide on Si, which is electrically insulating and hinders electroplating.

In this paper, we report our recent results on electroplating of Al on Si substrates in an above-room-temperature ionic liquid. Dense and adherent Al deposits have been reproducibly obtained directly on Si substrates from a 3:2 molar ratio AlCl_3 : EMIC solution at temperatures slightly above 100°C . In addition to structural and compositional characterization of the Al deposits, it is of great interest to examine their electrical properties for applications in metallization. The effects of deposition parameters such as pre-bake conditions, deposition temperature, and post-deposition annealing on the sheet resistance of the deposits were investigated. The resistivity of the Al deposits after annealing was in the high 10^{-6} Ω -cm range, similar to that of screen-printed silver (Ag) from an Ag paste. This electroplating process has been integrated into the fabrication of a wafer-Si solar cell for n-side metallization [17].

2. Experimental

We prepared the electroplating solution and conducted Al electroplating in a dry nitrogen box with a continuous nitrogen flow, which prevents the ionic liquid from absorbing moisture. All the chemicals, $(\text{EMIM})\text{AlCl}_4$ ($\geq 95\%$, Aldrich) and anhydrous AlCl_3 powder (99%, Aldrich), were used as received. The electroplating solution was prepared by mixing 3:2 molar ratio of AlCl_3 and $(\text{EMIM})\text{AlCl}_4$ in a dry beaker with continuous magnetic bar stirring at ambient temperature, ensuring Lewis acidic property. On completion of the room temperature mixing, a pre-bake was performed in which the obtained electrolyte was heated to different temperatures for different times in order to drive out the residual moisture in the electrolyte. Then, the temperature of the electrolyte was changed to a predetermined temperature for Al deposition.

The effect of pre-bake conditions and deposition temperature was investigated through the sheet resistance of the resultant Al deposits.

A three-electrode electrochemical cell was employed for all the experiments. Textured Si wafers, either n-type or p-type with resistivity between 0.3–1 Ω -cm, were used as the substrates. A thin SiN_x layer was deposited on the backside of the Si wafer to ensure one-side Al deposition. Prior to electroplating, the Si wafer was cleaned in diluted hydrofluoric acid (HF) to remove native oxide on Si surface. Al wires of 99.99% purity were used as the sacrificial anode and reference electrode. This makes the electroplating solution reusable for many deposition runs, as the Al anode supplies Al to the solution and keeps the Al concentration in the solution constant. The Al wires were cleaned with a short dip in 37% hydrochloric acid (HCl), followed by a deionized (DI) water rinse. After cleaning, the Al wires and the Si wafer (as the cathode) were immediately assembled and then transferred to the dry nitrogen box. The deposition of Al was performed at a temperature near the boiling point of water, and the electrolyte was magnetically stirred. The electroplating process was carried out galvanostatically, i.e. under a constant current of $\sim 15 \text{ mA/cm}^2$ for half an hour. After deposition, excess ionic liquid was removed from the sample by dipping it in absolute alcohol. The sample was then rinsed with DI water and dried with nitrogen. Post-deposition annealing under vacuum was also conducted to further reduce the sheet resistance of the Al deposits.

A scanning electron microscope (SEM) equipped with energy dispersive X-ray analysis (EDX) was utilized to examine the surface morphology and composition of the Al deposits. The crystal structure was studied with an X-ray diffractometer with Cu K α radiation. The sheet resistance of the Al deposits was measured with a four-point probe. The nominal thickness of the Al deposits was calculated by the following equation:

$$\text{Nominal thickness } (\mu\text{m}) = \frac{J(\text{A}/\text{cm}^2) \times t \times 27(\text{amu})}{96485 \times 3 \times 2.7(\text{g}/\text{cm}^3)} \times 10^4 \quad (1)$$

3. Results and discussion

Surface cleaning of the substrate prior to deposition is critical for Al electroplating. We used diluted HF to clean the Si substrate, which is effective enough to remove native oxide and leaves a clean Si surface for electroplating. It was found that whitish, dense, and adherent Al can be plated directly on Si if the resistivity of the Si substrate is below $\sim 1 \Omega\text{-cm}$. For Si substrates with $>1 \Omega\text{-cm}$ resistivity, the Al deposits were greyish and poorly adherent to the Si substrate. A seed layer of metal, such as nickel (Ni) or Ni silicide (NiSi), was required in this case.

Figure 1 shows top-view SEM images of Al deposits on a Si substrate and a NiSi-coated Si substrate at 70°C and $15 \text{ mA}/\text{cm}^2$ for 30 min without pre-bake of the electroplating solution. As shown in Fig. 1(a), the as-deposited Al film directly on the Si substrate is dense and reasonably homogeneous with large Al crystallites on the order of $10\text{--}20 \mu\text{m}$. For the NiSi-coated Si substrate which is used specifically for Si with $>1 \Omega\text{-cm}$ resistivity, the as-deposited Al film is dense with smaller crystallites on the order of $2\text{--}4 \mu\text{m}$ but more homogeneous than that obtained directly on Si, evidenced in Fig. 1(b). The increased homogeneity of Al on NiSi can be attributed to the fact that NiSi has a lower resistivity than Si, resulting in a more even current distribution in the substrate during electroplating. However, the adherence between NiSi and Al was so poor that the Al film could be easily peeled off regardless of surface preparation. Considering this material issue, the following results were obtained from Al deposits directly on textured n-type Si substrates with resistivity between $0.3\text{--}1 \Omega\text{-cm}$.

Figure 2 shows the corresponding EDX analysis and XRD pattern of the Al deposit in Fig. 1(a). In Fig. 2(a), the deposit displays only one strong peak of Al around 1.5 keV without any other peaks of different materials, suggesting a pure Al deposit under the conditions described. As shown in Fig. 2(b), all the four peaks of the deposit are related to Al and identified as Al(111), (200), (220), and (311), further confirming that the composition of the deposit is pure metallic Al.

The sheet resistance of electroplated Al was investigated. The effects of pre-bake conditions, deposition temperature, and post-deposition annealing conditions were examined. Three different temperatures (100, 120, and 140°C) and two different pre-bake times (30 and 60 min) were chosen as the conditions for moisture removal in the electroplating solution. After pre-bake, the solution temperature was changed to 70°C for a 30-min deposition at 15 mA/cm². Figure 3 shows the sheet resistances of Al deposits as a function of pre-bake temperature and time. The Al deposits show significant reduction in sheet resistance when the pre-bake temperature exceeds 100°C, which is the boiling point of water at one atmosphere. It was also noticed that the humidity level in the dry nitrogen box dropped from 19% to 16% after the electroplating solution was baked at 120°C for 60 min. This supports the assumption that the pre-bake drives out moisture from the solution. Moisture in the solution increases the possibility of aluminium oxide (Al₂O₃) formation in the Al deposit, which is an insulator and increases the resistivity of the Al deposit. It can be seen in Fig. 3 that the lowest sheet resistance is obtained at 120°C for 60 min, which is then used as the pre-bake conditions for all the subsequent experiments.

Figure 4 shows the sheet resistance of Al deposits as a function of deposition temperature before and after vacuum annealing at 350°C for 20 min. All the Al deposits were obtained on Si substrates at 15 mA/cm² for 30 min, and their nominal thickness is ~9 μm based on the total charge accumulated during electroplating. It is clear that the sheet resistance decreases as the

deposition temperature increases. The exact reason is still under investigation. One possibility is that higher temperatures keep moisture out of the electroplating solution, reducing the amount of Al_2O_3 in the deposits. Another possibility is that higher temperatures increase the density of the Al deposits, making the resistivity closer to the bulk value.

As shown in Fig. 4, the sheet resistance of the Al deposits was slightly reduced by post-deposition annealing. This may have resulted from the fact that annealing at higher temperatures than the electroplating temperature further increased the density of the Al film. The minimum sheet resistance obtained is $\sim 8 \text{ m}\Omega/\text{sq}$ for $9\text{-}\mu\text{m}$ Al, corresponding to a resistivity of $\sim 7 \times 10^{-6} \Omega\text{-cm}$. It should be noted that the nominal thickness of the Al deposits was calculated under the assumption of 100% current efficiency. In actuality, the current efficiency should be around 80–90%, meaning that the real thickness of the deposits should be lower than the calculated thickness. Therefore, the actual resistivity of the Al films could be lower than $\sim 7 \times 10^{-6} \Omega\text{-cm}$.

4. Conclusions

It has been shown that dense and adherent Al deposits with low electrical resistivity can be obtained directly on Si substrates by electroplating over a wide range of temperatures using galvanostatic deposition. Electroplating conditions such as pre-bake conditions, deposition temperature, and post-deposition annealing affect the electrical resistivity of the Al deposits. For reliable and low-resistivity Al deposits, the pre-bake and deposition temperatures should be above 100°C . The resistivity of electroplated Al is in the high $10^{-6} \Omega\text{-cm}$ range, similar to that of screen-printed Ag. The maximum process temperature for electroplated Al is well below 400°C . This makes Al electroplating a promising metallization method for Si solar cells and microelectronic devices.

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Figure captions

Figure 1. Top-view SEM images of Al deposits on (a) a Si substrate with resistivity below 1 Ω -cm and (b) a NiSi-coated Si substrate at 70°C and 15 mA/cm² for 30 min without pre-bake of the electroplating solution.

Figure 2. (a) EDX spectrum and (b) XRD pattern of an Al deposit obtained on Si substrate with resistivity below 1 Ω -cm at 70°C and 15 mA/cm² for 30 min without pre-bake of the electroplating solution.

Figure 3. Sheet resistance of Al deposits as a function of pre-bake temperature after 30- and 60-min pre-bake.

Figure 4. Sheet resistance of Al deposits as a function of deposition temperature before and after vacuum annealing at 350°C for 20 min.

Figures

Figure 1

Figure 2

Figure 3

Figure 4