Research Paper

Rapid Thermal Annealing at the Temperature of 650°C Ag Films on SiO₂ Deposited STS Substrates

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Abstract Flexible opto-electronic devices are developed on the insulating layer deposited stainless steel (STS) substrates. The silicon dioxide (SiO₂) material as the diffusion barrier of Fe and Cr atoms in addition to the electrical insulation between the electronic device and STS is processed using the plasma enhanced chemical vapor deposition method. Noble silver (Ag) films of approximately 100 nm thickness have been formed on SiO₂ deposited STS substrates by E-beam evaporation technique. The films then were annealed at 650°C for 20 min using the rapid thermal annealing (RTA) technique. It was investigated the variation of the surface morphology due to the interaction between Ag films and SiO₂ layers after the RTA treatment. The results showed the movement of Si atoms in silver film from SiO₂. In addition, the structural investigation of Ag annealed at 650°C indicated that the Ag film has the material property of p-type semiconductor and the bandgap of approximately 1 eV. Also, the films annealed at 650°C showed reflection with sinusoidal oscillations due to optical interference of multiple reflections originated from films and substrate surfaces. Such changes can be attributed to both formation of SiO₂ on Ag film surface and agglomeration of silver film between particles due to annealing.

Keywords: Ag agglomeration, Silicon dioxide, Rapid thermal annealing, Stainless steel

I. Introduction

Noble silver (Ag) thin films are very attractive materials for applications in flexible optoelectronic devices such as optical scattering layer and reflective metal electrode [1,2]. Therefore, Ag films have been intensively studied as they are easy to produce and have unique optical properties [3,4]. In previous researches, it is found that the surface roughness, and the size and shape of Ag nanoparticles will affect the optical properties of Ag films [5-7]. Many researches have been conducted to the preparation and stabilization of Ag nanoparticles in order to control their sizes, shapes, and distribution [5,8]. In recent years, it is found that the component of substrate also affect the sizes, shapes, and distribution of Ag nanoparticle. Ag layers can be formed by various methods such as thermal evaporation [9,10], electron beam (E-beam) evaporation [11], pulsed laser deposition [12], chemical vapor deposition (CVD) [13], electro-deposition [14], direct current sputtering [15-17], and resonant frequency sputtering [18,19]. Among these deposition technologies, the e-beam evaporation technique has been selected to fabricate the Ag thin films on stainless steel (STS) substrates, which are widely used

for flexible devices owing to chemical stability and low thermal expansion coefficient.

It was found that the diffusion of Fe and Cr atoms from STS substrates inhibit Ag agglomeration during the annealing process [20]. Also, a silver oxide can be formed by a rapid thermal annealing process of Ag films. In this work, it was studied the formation and application of Ag layer on silicon dioxide (SiO₂) deposited STS sheets annealed at 650°C using rapid thermal annealing (RTA) method.

II. Experimental Details

The STS substrates, which did not have a polishing treatment of surface for the confirmation of commercial usage, were cleaned by removing any organic contaminations using conventional method. And then, the RF plasma cleaning was used to enhance the adhesion of deposited films on the STS substrate. The O₂ plasma treatment was conducted at an 80 W (RF power) and 800 mTorr. Next, Ag and SiO₂ were deposited sequentially by evaporating and chemical deposition. In other words, the SiO₂ layer of 1 μm was first deposited on STS by plasma enhanced chemical vapor deposition (PECVD). Then the Ag layer of 100 nm was deposited on SiO₂ without vacuum breaking. And then, rapid thermal annealing is performed at 650°C

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for 20 min. The detailed fabrication method was also reported in Ref. 20. The analytical methods are scanning electron microscopy (SEM), electron backscatter diffraction (EBD), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and atom probe tomography (APT). The optical properties of annealed Ag films were studied by spectrophotometer.

III. Results and Discussion

1. Film characterization

Noble metals such as Ag have been reported [21,22] to grow on oxide surfaces in 3D island shape. Figure 1(a) shows the SEM image of Ag film grown on SiO_2/STS structures. The Ag film exhibits a small island growth with a grain size from 30 nm to 350 nm. It is possible to mention that even if the Ag layer grows from Volmer-Weber mechanisms, the grain density is higher and the grain texture is smaller. Also, voids is not detected between adjacent grains that form a dense and continuous Ag film. The distribution graphs of grain sizes with 100 nm

(a)

(b)

Figure 1. (a) SEM plane-view image and (b) electron backscatter diffraction (EBSD) distribution graphs showing surface grain sizes of as-deposited film on SiO_2 deposited stainless steel substrates.

thickness are provided in Fig. 1(b) in order to check the grain stack during deposition. The grain sizes are convergence, and the grains over 400 nm are not existed.

Figures 2 show the SEM image of the surface morphology of the specimen after RTA processing. The Ag

Figure 2. SEM plan-view images of Ag films on SiO_2 deposited stainless steel substrates after the annealing process at 650°C. The red line marks the location of the concentration profile, Fig. 5.

(a)

(b)

Figure 3. Concentration depth profile with respect to (a) as-deposited and (b) annealed Ag films on SiO_2/STS structures. Secondary ion counts for oxygen, silicon, chromium, iron, and silver are plotted against the sputtering depth.

Figure 4. XPS spectra of Ag films annealed at 650°C in the range of 0-800 eV.

film shape depended largely on the annealing temperature. The maximum annealing temperature is the important factor while the annealing time is normally kept as constant. Large agglomerates of non-continuous films transform into a cluster array, where each cluster is separated and it is not in contact with the neighboring clusters. It could be presumed that the presence of some atoms in Ag film was deduced by the out-diffused detrimental element from SiO₂ layer or STS substrate. The SIMS analysis is conducted in order to investigate the chemical reaction with Ag film by the diffusion of atoms on the annealing temperature. Figure 3 shows the SIMS element profiles to present the concentrations of various atoms including Ag, Si, O, Fe, and Cr after the annealing process. The movement of Si, O, Cr, and Fe signals towards Ag film surface is related with the annealing temperature. It means that the maximum concentration positions of the in-diffused Si, O, Cr, and Fe in Ag layer have shifted away from the SiO₂ surface. However, this is not sure for the reason as mentioned above. The phenomenon will be observed further with the other technique.

XPS analysis was conducted to investigate the surface composition of the synthesized composites as shown in Fig. 4. The XPS peaks show the elements of Ag, O, and Si in the sample. It is concluded that the Fe and Cr did not exist around the surface of Ag or SiO₂ layer. The existence of two characteristic peaks (Ag3d at 368.15 and 374.15 eV) indicates the incorporation of the Ag. According to the literature data [20,21], the photon energy range near 531 eV is attributed to oxygen 2p orbitals hybridized with the silver 4d character. So, it said that Ag4d orbitals contribute to the O-Ag bond for the nucleophilic oxygen. Also, the Si2p at approximately 102 eV peak is related with the presence of silicon oxide [22].

Based on the XPS result, we additionally performed APT analysis for investigating the detailed distribution of Si, O, and Ag atoms in a discontinuous Ag island. APT is analysis technique for both 3D imaging and chemical

(a)

(b)

Figure 5. (a) Specimen prepared into a tip for atom-probe tomography (APT) analysis. A carbon capping layer has been deposited at the tip. (b) Three dimensional reconstruction with isoconcentration surfaces of oxygen, silicon, and silver for the Ag sample annealed at 650°C (See the red line mark in Fig. 2).

composition measurements at the atomic scale (around 0.1-0.3 nm resolution in depth and 0.3-0.5 nm laterally). The measurement were carried out with a dual and focused ion beam using a UV laser ($\lambda = 343$ nm). Duration time and repetition rate of the laser are 500 fs and 100 kHz, respectively. Instrument base pressure was 10^{-10} Torr. The samples were prepared into a tip, as shown in Fig. 5(a). The measured area of 20×20 nm² is indicated by a dotted red-line in Fig. 2. The depth from the surface is 35 nm. Figure 5(b) shows the concentration distribution of Ag, O, and Si atoms in the sample. However, some interdiffusion of Si atoms, probably along the domain boundaries in the

silver oxide layer has taken place. Our results make it clear that at least Si atoms must be in annealed Ag films.

2. Electrical and optical properties

In order to further study the underlying electronic transport properties of Ag thin films, we fabricated Al/Zinc Oxide (ZnO)/Ag annealed at 650°C/Al structures as shown in Fig. 6(a). The diode device was processed as follows. After the annealing of Ag films, the lift-off technique using a photolithography method was performed to deposit n-type ZnO layer of 0.4 μm . Next, the Al (1 μm) metal was formed by photolithograph and sputtering processes. It is well known that Al and ZnO are ohmic and schottky contact materials for silver oxide, respectively [26,27]. And the contact between Al and ZnO is ohmic [28]. Figure 6(b) shows the reverse and forward bias current-voltage (I-V) characteristics of the annealed Ag film, based on two-probe devices. The result confirms that the annealed Ag layer have a p-type semiconductor behavior. The Al/ZnO/Ag annealed at 650°C/Al structures have the performance of a Schottky diode. Based on these results, the low

temperature (15 K) photoluminescence (PL) spectrum was measured to determine the optical bandgap energy (E_g) for annealed silver films. Figure 7(a) shows the PL data dominated by two peaks ($\lambda = 1224$ and 1237 nm). Therefore, the annealed Ag film can be identified around the bandgap energy (~ 1 eV). It is well known that a Ag_xO film with a wide energy bandgap from 1.1 to 3.4 eV can be deposited using magnetron sputtering [29-31], chemical bath deposition [32], electrodeposition [33], electron cyclotron resonance O_2 plasma assisted e-beam evaporation of Ag [34,35], *etc.* The wide energy band gap range is due to the different stoichiometries, crystalline phases, and properties arising from different deposition methods. However, our current result containing Si and O atoms in Ag films is different from the results reported in the literature. The transport and binding mechanism of Si atoms in annealed Ag thin films on STS substrates should be investigated further in the future.

Ag films due to their noble optical properties have attracted much attention [36-38]. In previous reports, the size and shape of silver nanoparticles affect the optical

(a)

(b)

Figure 6. (a) Schematic diagram of Al/ZnO/Ag annealed at 650°C/Al structures for estimating the electrical property of Ag films and (b) I-V characteristics of the diode device for the structure of (a).

(a)

(b)

Figure 7. (a) Low temperature photoluminescence spectrum for Ag films annealed at 650°C. (b) Reflectance as a function of wavelength for as-deposited and annealed Ag films.

properties of Ag films [39]. Therefore, we have applied the reflectance measurement for coated materials on metal foil. Figure 7(b) shows the total reflectance of as-deposited and thin films for 20 min annealed at the temperature of 650°C. The reflectance is high in the near infrared wavelengths, then it decreases in the visible region, and drops considerably into the ultra-violet one. The high absorption peak at ~320 nm, typical for pure Ag [40], was observed only for relatively thin films (100-150 nm). Also, the absorption peak around 350 nm and its tail are due to the surface plasmon resonance of Ag. The films annealed in 650°C show low reflection with sinusoidal oscillations. The oscillations in the reflectance spectra are caused by optical interference of multiple reflections originated from films and substrate surfaces. Such changes can be attributed to the Ag particles formation and gaps between particles due to annealing process, as seen in SEM images of Fig. 2.

IV. Conclusions

In this study, post-annealing at 650°C for 20 min varied the film structure (size and shape) of the thin film with a constant thickness. We found that the movement of silicon atoms, along the domain boundaries in the Ag layer has taken place. During annealing, the interaction of interlayer plays an important role for the formation of the surface morphology.

Optical and electrical properties of the films were also investigated. Al/ZnO/Ag annealed at 650 °C/Al diodes have been fabricated on SiO₂/STS substrates. Film annealed at 650°C had the material property of p-type semiconductor and the bandgap of approximately 1 eV. A general trend is that a broader absorbance can be found for annealed films. In addition, the films annealed at 650°C showed reflection with sinusoidal oscillations due to optical interference of multiple reflections originated from films and substrate surfaces. Such phenomenon can be attributed to the diffusion of Si atoms in silver film on SiO₂ deposited STS substrates during annealing.

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