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Effects of rapid thermal annealing for E-beam evaporated Ag films on stainless steel substrates

Moojin Kim [a], Kyoung-Bo Kim [b,*,1], Dongyun Lee [c], Sung-Nam Lee [d], Ji-Myon Lee [e]

[a] *Department of Renewable Energy, Jungwon University, Goesan-gun, Chungbuk 367-805, Republic of Korea*
[b] *POSCO Technical Research Laboratories, Songdo-dong, Yeonsu-gu, Incheon 406-840, Republic of Korea*
[c] *Department of Nano Energy Engineering, Pusan National University, Busan 609-735, Republic of Korea*
[d] *Department of Nano-Optical Engineering, Korea Polytechnic University, Siheung 429-793, Republic of Korea*
[e] *Department of Printed Electronics Engineering, Sunchon National University, Sunchon, Chonnam 540-742, Republic of Korea*

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ABSTRACT

There is significant interest in the development of flexible substrates for making electronic devices such as solar cells and organic light emitting diodes using roll-to-roll processes. Stainless steel (STS) is commonly used for flexible substrates. To explore the potential for new STS applications (e.g., optical scattering layers in opto-electronic devices) silver thin films of ~100 nm thickness were deposited on STS substrates using the thermal evaporation technique. The films then underwent rapid thermal annealing (RTA) to create various sizes of silver particles. The RTA method was carried out at annealed temperatures from room temperature (RT) to 550 °C for 20 min. We investigated variation of the surface morphology caused by the interaction between Ag films and STS substrates after the RTA annealing. The grain size was studied by using scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) methods. When the film was annealed at 250 °C, particles started to separate and the gaps between particles enlarged. However, at the high temperatures (450 and 550 °C), we observed that the gaps decreased when the annealing temperature was increased from 350 to 550 °C. In particular, the surface of STS substrate was completely covered with Ag particles for the film annealed at 550 °C. The results showed the suppression of the agglomeration of the Ag film. Secondary ion mass spectroscopy (SIMS) and X-ray photoelectron spectroscopy (XPS) was used to examine the movement of Fe and Cr atoms in silver film from STS substrates. These atoms observed with SIMS and XPS must be at the surface. It was found that Fe and Cr atoms play a critical role in suppressing Ag agglomeration.

The optical properties of annealed Ag films were studied by spectrophotometer. Broader absorbance was found for films with 450 °C annealing temperature. The total reflectance of the Ag films annealed at 550 °C increased over the wavelength range of 400–800 nm, compared with that at 450 °C. This was due to suppression of Ag agglomeration.

1. Introduction

Nano-scaled materials such as metal, dielectric, or composites of metal-dielectric film have attracted great interest in modern technology due to their structural, optical, and electrical properties. In particular, noble metal films (e.g., gold (Au), platinum (Pt) and silver (Ag) [1–4]) have a wide range of applications in modern electronic and photonic systems, including catalysis [5], optics [6], and bio-sensing [7]. In addition, silver thin films have been extensively studied as they are easy to prepare and have novel optical properties [8,9]. The size of the Ag particles plays an important role in tuning the properties for the exact technical need [10]. A number of techniques such as RF magnetron sputtering, ion implantation, and E-beam evaporation have been used to deposit Ag films. In particular, E-beam evaporation techniques have been shown to provide better coating uniformity under given deposition conditions. Rapid thermal annealing (RTA) is commonly used, rather than the conventional thermal annealing process, to improve throughput properties for mass production. This is because the ultrafast annealing time does not affect the device properties when the film is used in devices [11–14]. There are also many recent reports on the effect of annealing on silver films using the RTA process [15]. In addition, silver films on dielectric materials have been studied. This involved the surface morphology of silver films formed by RF sputtering (or by E-beams) at different temperatures [16,17].

Stainless steel (STS) and polymer substrates are commonly used for flexible devices in roll-to-roll processes [18–20]. In particular, STS substrates have advantages such as chemical stability and lower

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[*] Corresponding author.
E-mail address: heli111@naver.com (K.-B. Kim).
[1] Present Address: Korea National Cleaner Production Center, Korea Institute of Industrial Technology, Seoul 135-918, Republic of Korea.

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thermal expansion coefficients, compared with polymer substrates. Furthermore, a higher temperature process is possible due to the higher thermal stability of STS, and a passivation layer is not required in order to prevent water vapor and oxygen from moving through the substrate.

In this work, Ag films were deposited on STS substrates by electron beam (E-beam) evaporation. We studied the formation of Ag/STS structures as a result of varying the annealing temperature using the RTA method. The surface morphology of the Ag layers can be modified by tuning the process parameters. For the first time, we discovered the out-diffusion of Fe and Cr atoms caused by chemical reaction between Ag films and STS substrates at high annealing temperatures. The suppression of agglomeration is also discussed for the present system. The surface morphology of the films was examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS), electron backscatter diffraction (EBSD), X-ray photoelectron spectroscopy (XPS), 3D profiler, and UV–vis spectrophotometer.

2. Experimental details

For this experiment, STS (Cr steel) with a thickness of 127 μm (already commercialized for use in a thin-film solar cell by POSCO) was used as a substrate because the thermal expansion coefficient of Cr steel (10.5 ppm/K) is lower than that of nickel (Ni)–Cr steel (15.0 ppm/K) [21,22]. The STS sheets were prepared for the deposition of Ag layers. All samples were cleaned strictly according to the following procedure before the deposition in order to ensure a good adhesion between the substrate and the thin film. An ultrasonic cleaning with organic solvents and de-mineralized water in a Class 100 clean-room was performed on each substrate. The processes occurred during ultra-sonication to thoroughly remove grease and organic contamination. Then, steel sheets were dried with nitrogen. After solvent cleaning, O_2 plasma treatments using reactive ion etching were also performed to remove possible surface contamination prior to metal deposition. The parallel plate plasma was formed from oxygen gas. It was reported that O_2 plasma treatments have a surface cleaning effect [23]. Next, the Ag thin film of 100 nm was prepared on STS substrates by the E-beam physical vapor evaporation method, as shown in Fig. 1. The advantage of E-beam deposition is that it limits the heating of the material to a small area of the bulk material avoiding problems related to the over-heating of the crucible, and the possible alloying between the bulk and the crucible material. Considering these aspects, the E-beam evaporation technique was selected to obtain the silver films. The equipment used in this work was composed of an evaporator and a 150 keV ion accelerator in the same chamber; so that the coating and ion beam processes could be conducted in situ without breaking the vacuum. The base chamber pressure was ~1×10^{-7} Torr and the operational pressure during E-beam deposition was ~5×10^{-5} Torr. The substrate was maintained at room temperature (RT). The deposition rate was monitored using a quartz crystal thickness monitor. Then, rapid thermal annealing was performed to treat samples, completing the actual fabrication process. RTA experiments were performed in a heating chamber interfaced with an integrated computer control system. Two identical rows of tungsten-halogen lamps (one above and one below the sample holder) were used to uniformly heat the disk sample. The temperature at the sample surface was measured by a thermocouple placed in contact with the backside of the sample holder. Due to the symmetrical heating, the measured temperature was equal to that at the film surface. The accuracy of the temperature measurement was within 2 °C. The heating rate during RTA was set at 8.5 °C/s. Because of the short duration of heating, the temperature measured by the thermocouple was slightly different from the set temperature. A typical temperature profile of the RTA treatment was obtained from thermocouple measurements. Hereafter, temperature will always refer to the temperature measured by the thermocouple. The base chamber pressure was ~1×10^{-4} Torr. In this work, heating to one of five temperatures (150, 250, 350, 450, and 550 °C) for 20 min was conducted in order to have Ag particles of different sizes. The analytical results provide evidence that the annealing greatly affected the final surface morphology of Ag thin films, as explained in the next section.

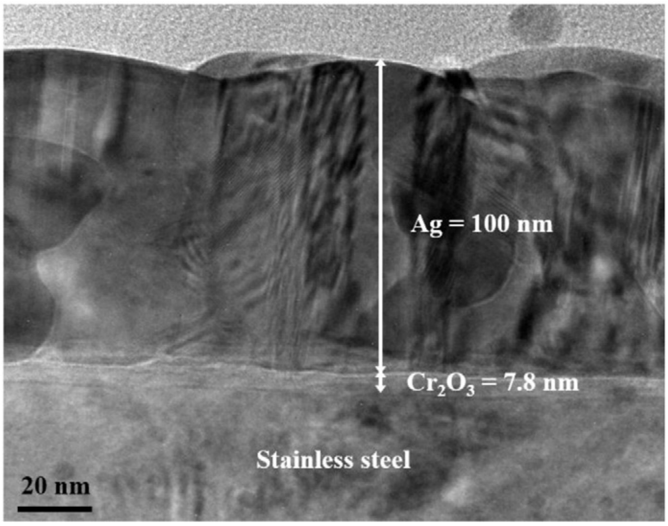

Fig. 1. TEM micrograph showing the cross section of Ag/Cr_2O_3/STS structure. The thickness of the Ag and Cr_2O_3 layers is 100 and 7.8 nm, respectively.

3. Results and discussion

3.1. Film characterization

Silver and the noble metals in general, have been reported [24,25] to grow on oxidized surfaces in 3D island mode. As shown in Fig. 1, the surface of STS sheets is passivated by chromium oxide to protect the steel bulk from oxygen or water vapor in the air. Then, the successive growth is governed by the accumulation of Ag atoms during surface diffusion and coalescence into clusters (Volmer–Weber growth mode) [6,26]. The boundary between the oxide layer and the Ag bulk was sharp and an interface with finite thickness was observed. The SEM image of Ag film grown on Fe–Cr steel sheets is shown in Fig. 2(a). The Ag layer exhibited a small island-growth with a grain size in the range 30–250 nm. There were also no voids observed between adjacent grains. In order to examine the grain stack during deposition, the distribution graphs of surface grain sizes are provided in Fig. 3(a). The grain sizes were convergent, and there were no grains > 300 nm. At the early stages, where the film is extremely thin, it consisted of isolated, compact islands. As deposition proceeded, the latter grew and became larger, but were still compact islands. When the film reaches a certain thickness, these islands coalesce into near equilibrium compact shapes forming percolating structures. Finally, the channels between the structures are filled in and a continuous surface, free of holes, is created.

Figs. 2(b–f) and 3(b–f) show SEM images and distribution graphs of the sizes of surface grains of the specimen after RTA processing. The annealed Ag layer shows a very irregular and isolated hole morphology, which could be explained by the high rate of surface diffusion of Ag atoms in the oxygen-containing ambient [27]. A lot of small particles around 30 nm are shown. These are presumably attributable to the relief of mechanical stress and surface oxidation effect. The Ag film morphology depends largely upon the annealing temperature. The temperature is the most important factor in annealing, while the duration of heating is normally kept constant. Based on the dependence of gap size between particles on annealing temperatures, we were able to distinguish two regions.