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Effect of annealing on morphology, optical reflectivity, and stress state of Al–(0.19–0.53) wt.% Sc thin films prepared by magnetron sputtering

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ABSTRACT

Degradation caused by formation of hillocks is a problem when traditional aluminum thin film acts as the reflector of the novel automobile lamp in which light emitted diode (LED) serves as the light source. This degradation in lamp performance is attributed to the annealing effect caused by cyclic change of temperature. Thin Al–0.19–0.53 wt.% Sc alloy films prepared by magnetron sputtering are potential candidates for substituting pure aluminum films as the reflector due to their excellent optical reflectivity and corrosion resistance. The annealing effect on the morphology of Al–Sc thin films arisen from thermal cycle during the service of auto lamps is of interest. The films were heated from room temperature to 450 °C and cooled down to examine their surface morphology. Hillocks on the pure Al film could be dramatically reduced in Al–0.19–0.48 wt.% Sc films and their formation was completely inhibited in Al–0.53 wt.% Sc. Examination through scanning electron micrographs (FE-SEM) reveals that Al–0.53 wt.% Sc comprises nano grains that are much finer than those in other films. According to stress analysis on the film, we proposed a mechanism for interpreting the formation of hillocks on the Al film and their inhibition on Al-Sc films. Al–0.53 wt.% Sc thin film is suggested to be a candidate for reflectors in a LED auto lamp.

1. Introduction

Thin aluminum film has been regarded as a good reflector in traditional automotive lamps because of their high optical reflectivity and its ease of fabrication. Thermal evaporation is the main technique for preparing the Al-film reflector due to the lower melting and boiling points of aluminum relative to other metals. Approximately 80–85% of optical reflectivity is determined by the quality of the reflector film. Optical reflectivity was reported to decrease drastically due to hillock formation when the reflector has been annealed in a high-temperature environment such as the hood of vehicle [1]. In our earlier work, we found that sputtered Al–0.11 wt.% Sc film reveals better characterization (i.e., film adhesion, optical reflectivity, and anti-corrosion behavior) compared with the evaporated pure Al film when used as the reflector of auto lamp [2].

The role of scandium in Al–Sc films is interesting. It has been known that alloying of Sc into aluminum strengthens the mechanical properties of the metal. The strengthening is attributed to grain refinement and a rise in recrystallization temperature [3–7]. Cavanaugh et al. [8] studied the electrochemical characteristic of Al–Sc alloys in dilute chloride solution. They found that the precipitates Al_3Sc display good electrochemical compatibility with Al substrate so that Al–Sc alloys reveal good resistance to corrosion.

It is interesting to investigate the effect of annealing on the morphology of Al–Sc films with Sc content ranging from 0.19 to 0.53 wt.%. The purpose was to find out the optimal Sc content in Al–Sc films to prevent the possible annealing effect caused by the LED light source.

2. Experimental procedure

The Al film was thermally evaporated in the vacuum chamber but Al–Sc films were deposited by sputtering on the silicon substrate. In the sputtering chamber, the pressure was initially controlled at 10^{-6} Torr, purged with argon gas to 3×10^{-3} Torr and then set out to deposition. Various Al–Sc alloying targets were prepared by melting 4 N Al and Al–1.7 wt.% Sc alloy. DC power (90 W for 90 min) was employed in the sputtering process.

The stress exerted onto a thin film, in response to heating and cooling in a thermal cycle, was in situ measured by a curvature measurement system using a 7-mW He–Ne laser. The specimen was heated from 50 to 450 °C at a heating rate of 10 °C/min, and it was cooled naturally to room temperature.

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Table 1
The compositions of various Al–Sc thin films analyzed by ICP-OES.

Symbol of the film	Al (wt.%)	Sc (wt.%)
Al	99.99	–
0.19 Sc	99.81	0.19
0.22 Sc	99.78	0.22
0.48 Sc	99.52	0.48
0.53 Sc	99.47	0.53

The surface profile and roughness of the film were examined by an atomic force microscope (AFM, SHIMADZU, SPM-9500). The optical reflectivity of films was determined using a τ–ρ-meter (LMT Co.,) in which a standard light (ρ) illuminates on the specimen and the reflectivity is determined by an integrating sphere. Surface morphology of films was examined by a high resolution scanning electron microscope (SEM, FEI, NOVA Nano SEM 230). The composition of Al–Sc thin films was analyzed by EDS (Energy dispersive X-ray spectroscopy, Bruker QUANTAX EDX System). The films were dissolved in concentrated hydrochloric acid and subject to analysis by inductively coupled plasma (ICP-OES) emission spectrophotometer (JOBIN YVON JY24) for determining their composition.

3. Results and discussion

3.1. Composition and morphology of Al–Sc films

Table 1 displays the composition of various thin aluminum films with different Sc-contents (wt.%) at 0, 0.19, 0.22, 0.48 and 0.53 denoted as Al, 0.19 Sc, 0.22 Sc, 0.48 Sc and 0.53 Sc, respectively. Fig. 1 displays (a) the morphological examination by SEM on the cross-section and the corresponding (b) mapping of elements, and (c) EDS spectrum for Al–0.19 wt.% Sc film. The thickness of films was roughly at 3 μm and they revealed a homogeneous distribution of Al and Sc in the film. The presence of Sc in the films is evident according to the EDS in Fig. 1(c) although the mapping diffused extensively due to the dilute concentration of Sc.

For comparison, Fig. 2 depicts the FE-SEM morphologies for pure Al film (a) as-deposited and (b) annealed at 85, (c) annealed at 185 and (d) annealed at 450 °C for 1 h, respectively. It is obvious that there are several small hillocks (roughly 0.5 μm in diameter) present in both specimens (a) as-deposited and (b) annealed at 85 °C for 1 h. The occurrence of these small hillocks may be due to the accompanying heat carried by the thermal aluminum vapor. The hillocks grow their sizes up to 1.0 μm when the film has been annealed at 185 °C for 1 h, as shown in Fig. 2(c). The hillocks grow continuously into larger size

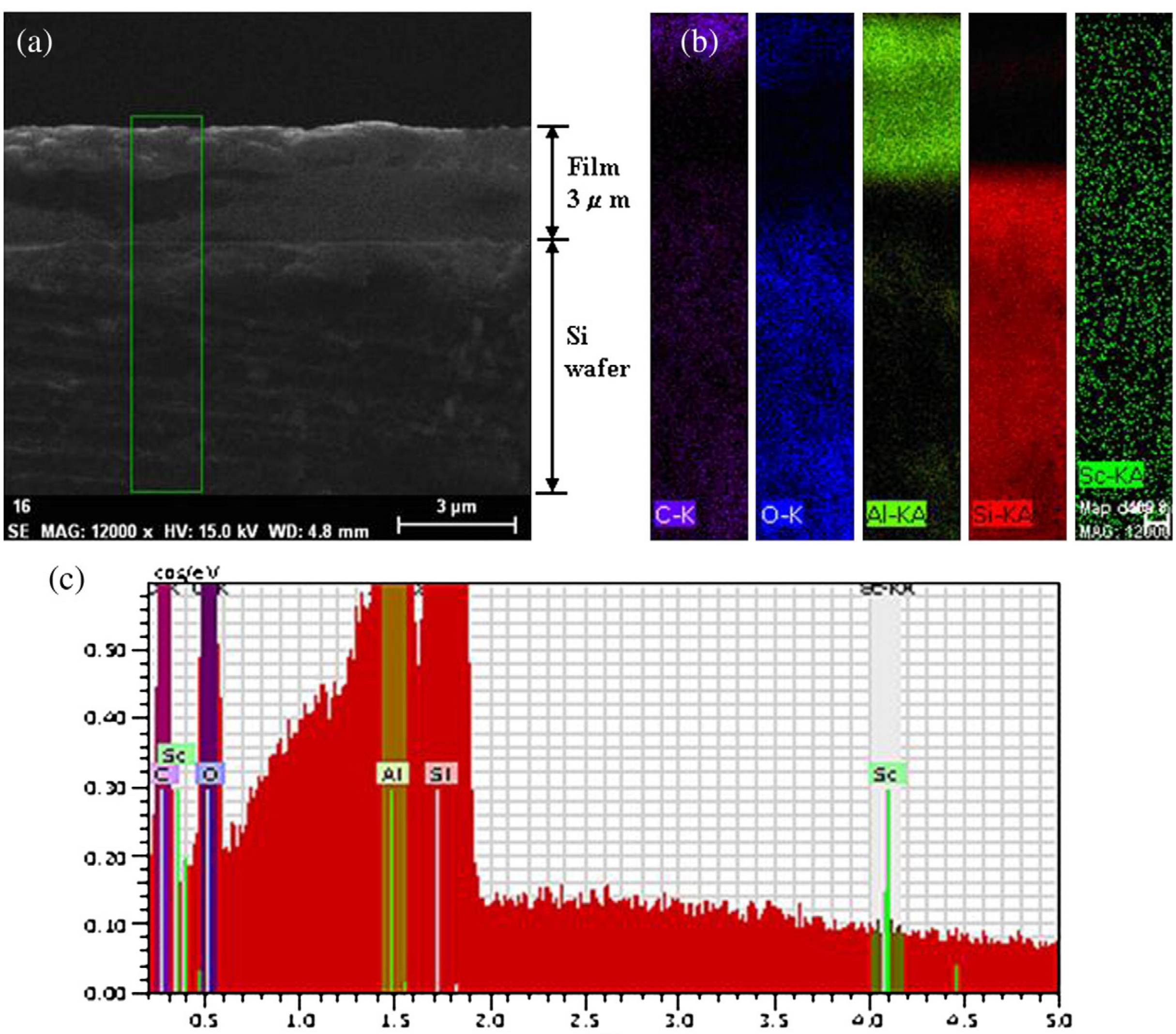

Fig. 1. (a) Cross section of SEM morphology, (b) mapping of C, O, Al, Si and Sc, and (c) EDS spectra for 0.19 Sc film.

(almost 2.0 μm in diameter) after their annealing at 450 °C for 1 h. There are a few cracks present on the hillock, making it a film defect. It is worth noting that films annealed at 450 °C turn into a denser structure showing good flatness except covered with a few large cracked hillocks.

Fig. 3 depicts the effect of Sc-content on the average grain size of the Al–Sc films. The SEM surface morphologies of pure Al film (a) and of Al–0.53 Sc film (b) are given for comparison. In Fig. 3, the grain size is 190 nm for the pure Al film. It decreases gradually to 165 nm with an increase of Sc-content from 0.19 to 0.48 wt.% and rapidly to 50 nm with Sc-content up to 0.53 wt.%.

Fig. 4 shows the FE-SEM morphologies for the annealed film containing 0.22 wt.% Sc (in Fig. 4a) and that containing 0.53 wt.% Sc (in Fig. 4b) also annealed at 450 °C for 1 h. It is evident that many hillocks (white spots) distributed on the surface of annealed film containing 0.22 wt.% Sc (Fig. 4a). In contrast, no hillocks could be found on the surface morphology of the annealed film containing 0.53 wt.% Sc (Fig. 4b). According to the results shown in Fig. 4, we inferred that 0.53 wt.% Sc is a critical concentration responsible for grain refinement and inhibition of hillocks formation on the films subject to annealing at 450 °C for 1 h.

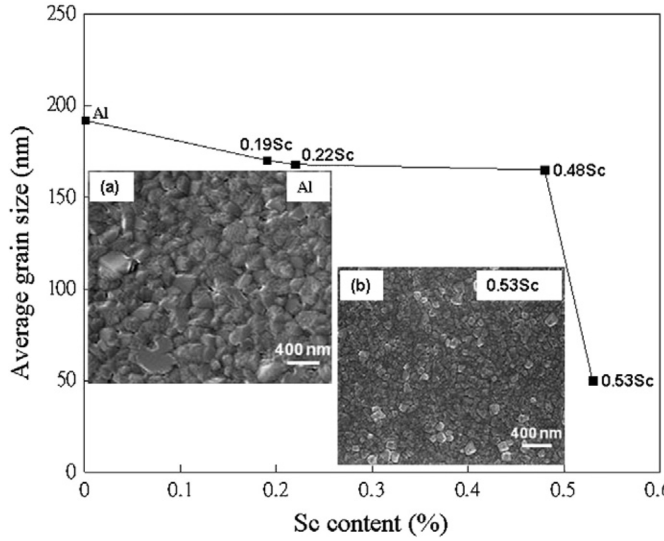

Fig. 3. Average grain size of the film as a function of Sc-content in the films. FE-SEM surface morphologies for (a) pure Al and (b) 0.53 Sc films are displayed.

3.2. Roughness on film surface

Fig. 5 shows the average roughness (Ra) and maximum roughness (Rmax) estimated by AFM measurements on the as-deposited films and those post-annealing at 450 °C for 1 h. The data of Ra and Rmax reveal that annealing at 450 °C for 1 h leads to an increase in roughness as compared to the as-deposited. Alloying of Sc into Al film

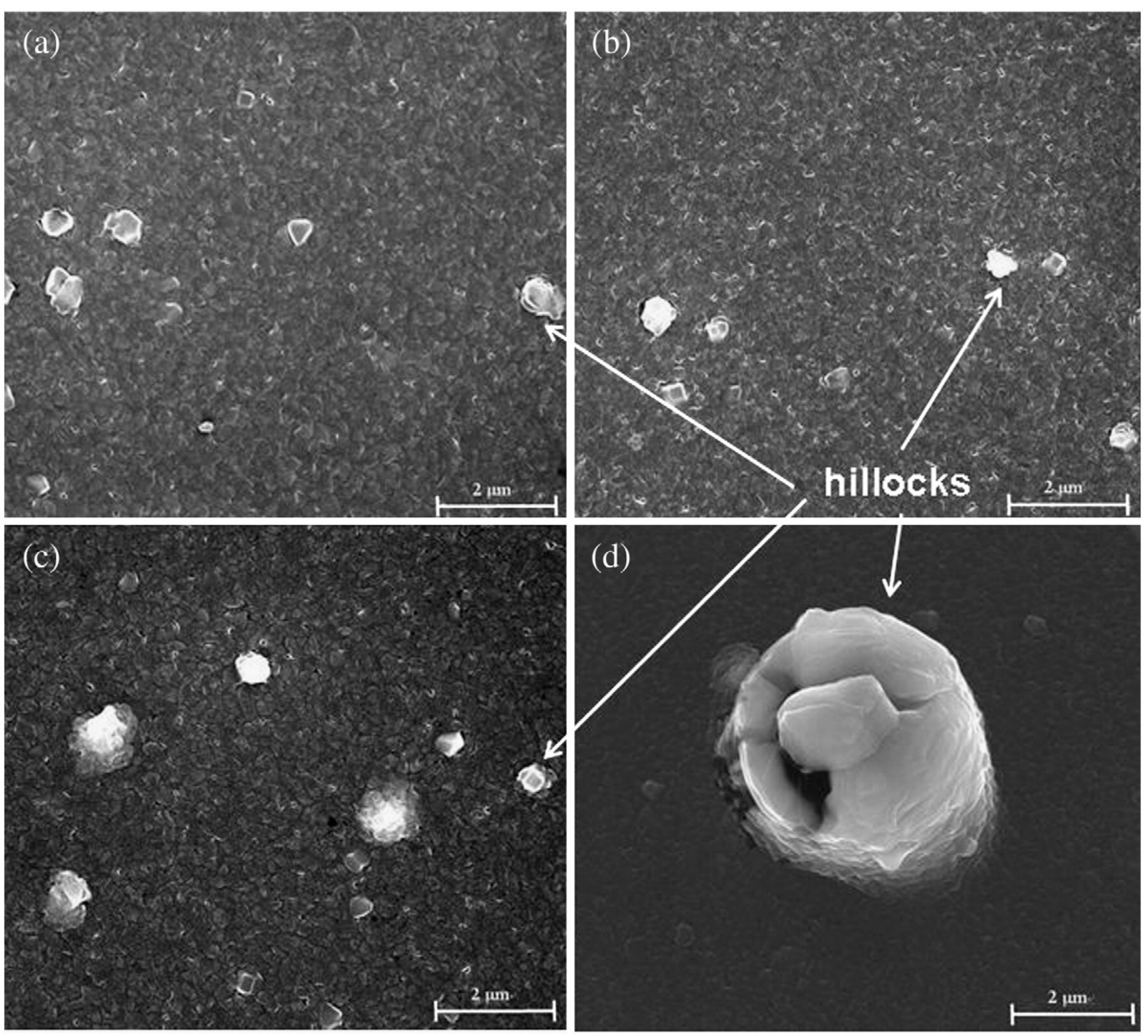

Fig. 2. The FE-SEM morphologies for Al film (a) as-deposited, (b) annealed at 85 °C for 1 h, (c) annealed at 185 °C for 1 h and (d) annealed at 450 °C for 1 h, respectively.

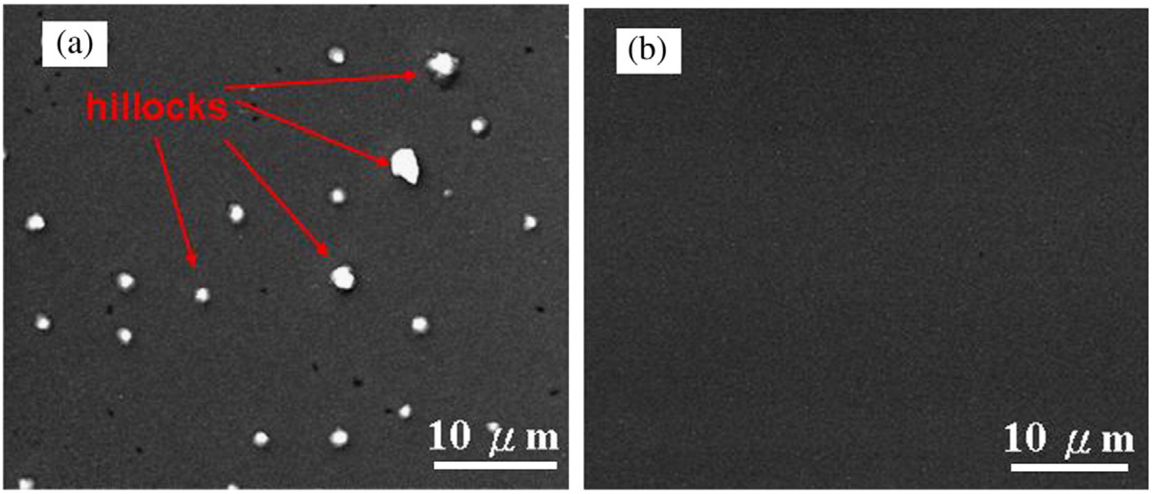

Fig. 4. Top view on the FE-SEM morphologies of (a) 0.22 Sc and (b) 0.53 Sc post-annealing at 450 °C for 1 h.

tends to decrease roughness except the case of Ra for as-deposited Al and 0.19 Sc films. In contrast to the as-deposited films, 0.53 Sc film reveals the lowest roughness (i.e., Ra = 4.73 nm, Rmax = 6.48 nm) while Al is the film with the highest roughness (i.e., Ra = 13.08 nm, Rmax = 13.58 nm). As seen in Fig. 2, annealing of films results in formation of hillocks. The increase in roughness may be ascribed to the occurrence of hillocks on the films. It is evident that roughness increases slightly for 0.53 Sc annealed at 450 °C for 1 h (i.e., Ra = 5.463 nm, Rmax = 7.854 nm); however, roughness increases prominently for pure Al annealed at 450 °C for 1 h (i.e., Ra = 23.47 nm, Rmax = 31.81 nm). Apparently, alloying Sc up to 0.53 wt.% leads to decrease in roughness of films while annealing leads to increase in roughness of films. The roughness of Al–Sc films only increases slightly after annealing as compared with that of the pure Al film.

Fig. 6 depicts the optical reflectivity for various Al–Sc films as-deposited and post annealed at 450 °C for 1 h. Among as-deposited films, 0.48 Sc film displays the highest reflectivity (at 84.1%). Comparing the data plotted in Fig. 6, one finds that all Al–Sc films maintain their reflectivity above 80%, which is much higher than that of pure Al film (at 56%). According to Fig. 4, one found that any film containing 0.53 wt.% Sc can prevent the formation of hillocks during its annealing at 450 °C. The film free from hillocks will lead to higher reflectivity when an optical light is illuminated. Further compared the data of Ra and Rmax plotted in Fig. 5, we found that the film containing higher Sc-content tends to have less roughness despite as-deposited or annealed. The film with less roughness is a smoother surface so that it has higher optical reflectivity during light emitting.

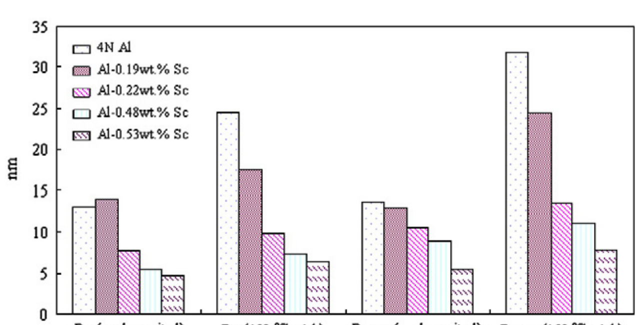

Fig. 5. A plot of Ra and Rmax data for as-deposited films and those annealed at 450 °C for 1 h. The Sc content in the films varying at 0, 0.19, 0.22, 0.48 and 0.53 wt.%.

3.3. Stress measurement of films

Fig. 7 displays a plot of stresses as a function of temperature in a thermal cycle heating from 50 to 450 °C, followed by natural cooling. The stress exerted on a thin film (F/W) was estimated by measuring the rate of curvature on the surface of specimen according to Stoney's equation.

$$F / W = \sigma_f \cdot t_f = \{E_s / [6 \cdot (1-\nu_s)]\} \cdot t_s^2 \cdot (K-K_0) \quad (1)$$

where

F	Force exerted on thin film.
W	Width of specimen.
σ_f	Stress of thin film.
E_s	Young's Modulus.
ν_s	Poisson's Ratio.
t_f	Thickness of thin film.
t_s	Thickness of substrate.
K	Rate of curvature measured from surface of specimen.
K_0	Initial rate of curvature measured from surface of specimen.

When the system is heated, a compressive stress (the data of force below the horizontal zero line in Fig. 7) is induced on the film. This stress increases to a maximum and decreases to almost zero with

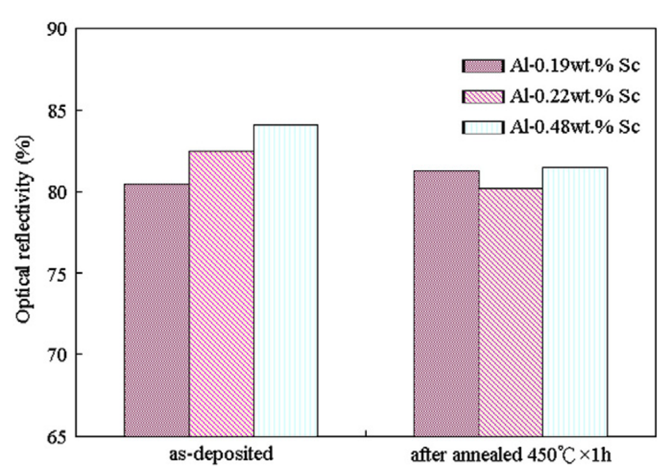

Fig. 6. Optical reflectivity for the as-deposited and annealed films varying the Sc-content at 0.19, 0.22 and 0.48 wt.%.

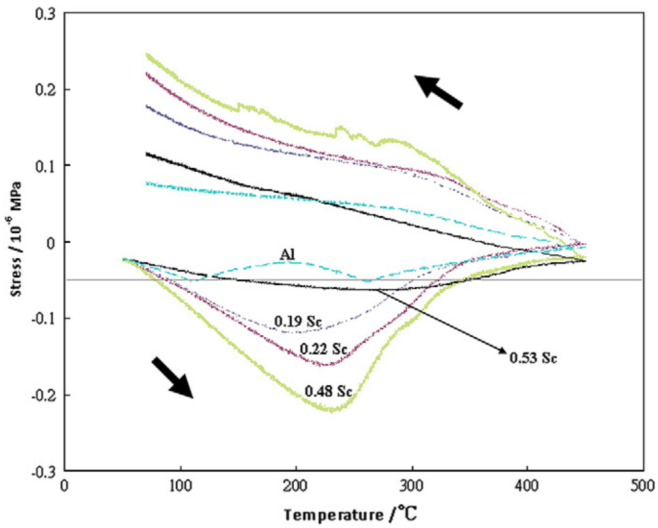

Fig. 7. Stress measured for the Al, 0.19 Sc, 0.22 Sc, 0.48 Sc and 0.53 Sc films heating from 50 to 450 °C and then cooled.

increasing the temperature from 50 to 450 °C. At the stage of natural cooling, a tensile stress is induced and it increases with decreasing temperature. As seen in the compressive stress curves, the maximal compressive stress increases with increasing Sc content from 0.19 to 0.48 wt.% in the films. It is worth noting that the maximal compressive stress induced in 0.53 wt.% Sc is much less than in 0.19 wt.% Sc and reveals a little higher than the pure Al film. The diminishment of compressive stress may be attributed to grain refinement in 0.53 Sc film which a lot of grain boundaries share the compression. On the other hand, the maximal compressive stress of the film reveals at different temperature depending upon the Sc-content. In Fig. 7, the temperature in response to maximal compressive stress decreases in the order: 0.53 Sc (290 °C)>0.48 Sc (225 °C)>0.22 Sc (220 °C)>0.19 Sc (190 °C)>Al (110 °C). It is reasonable that the strength of films with higher Sc-contents is stronger so that they are more resistant to induce compression. Specimen 0.53 Sc reveals the smallest compressive stress compared with all other Al–Sc film and it happens at the highest temperature (roughly at 290 °C). Due to this fact, it is very difficult to form hillocks in the film with 0.53 Sc. During the cooling stage, the tensile stress increases with decreasing temperature. Specimen 0.53 Sc indicates the smallest tensile stress than the other Al–Sc films. In the absence of hillocks, the surface of 0.53 Sc film is very smooth.

According to the results of surface morphology, roughness and optical reflectivity, the effect of annealing on the morphology could be illustrated with the schemes demonstrated in Fig. 8. The difference in thermal expansion coefficient of the thin film and substrate plays an important role. When a silicon system coated with Al or Al–Sc thin film is subject to heating, the expansion of the film arisen from a higher thermal expansion coefficient (linear thermal expansion coefficient at 23×10^{-6}/K for Al) is constrained by the substrate, which has a lower thermal expansion coefficient (linear thermal expansion coefficient at 2.6×10^{-6}/K for Si) [9]. This constraint by the substrate exerts a compressive stress onto the film. Size difference between the film and the substrate resultant from their different expansion coefficients tends to magnify with increasing temperature. At heating temperature higher than the recrystallization point of the film, vivid diffusion of Al atoms facilitates the formation of hillocks and releases the compressive stress. As reported in the literature [5], the Al–Sc system involves the precipitation of Al_3Sc particles, which retard the motion of dislocations and cause grain refinement. The higher the Sc concentration in the Al–Sc system, the denser the distribution of precipitates in the matrix is. Consequently, the mechanical property is stronger for Al–Sc containing higher Sc content. Comparing the size of grains in Al and that in Al–Sc, we find that the average size of grains in 0.19, 0.22 and 0.48 Sc films is roughly 160 nm, which is slightly smaller than in pure Al (about 190 nm); however, the size is much smaller in 0.53 Sc (i.e., 50 nm) than in other films. The temperature indicates that the release of compressive stress by formation of hillocks is closely related to the recrystallization temperature of the film. The increase in recrystallization temperature caused by higher Sc content leads to a rise in temperature responsible for formation of hillocks. This inference is consistent with the aforementioned result. Since 0.53 Sc has very fine nano grains (about 50 nm), there exists a lot of grains and grain boundaries that provide sites for damping of the stress. As a result, the maximal compressive stress induced in 0.53 Sc is much smaller than that in other Al–Sc films. The variation in tensile stress with cooling temperature could also be realized by considering the mechanical strength enhanced by Sc alloying in the Al film.

4. Conclusions

Annealing of Al–Sc films leads to different morphologies depending on their Sc content. Heating the Al and Al–Sc films coated on the silicon substrate gives rise to compressive stress. The compressive stress will be released by formation of hillocks at higher temperature. Hillock formation increases the surface roughness and decreases the

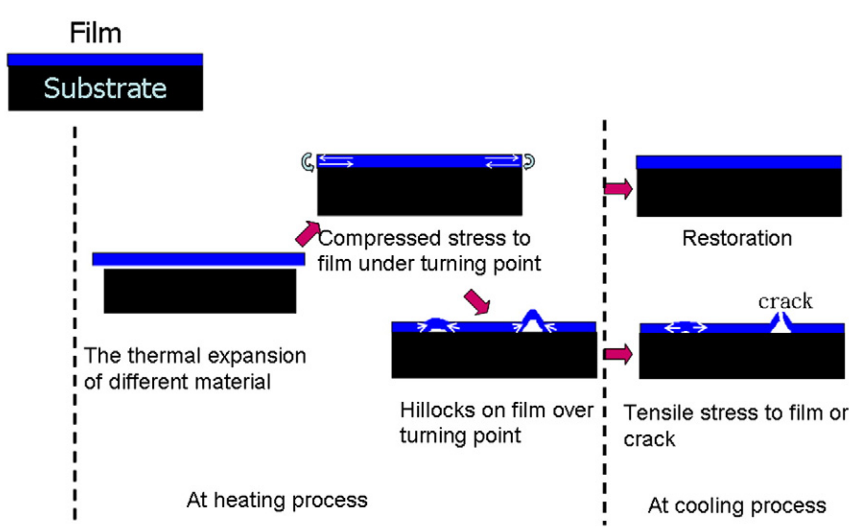

Fig. 8. A scheme to illustrate the stress caused by heating and cooling of the film. Hillocks are formed at the heating process and they tend to crack at the cooling process.

optical reflectivity of films. Film degradation caused by hillock formation could be prevented by alloying Sc at 0.19, 0.22, 0.48 and 0.53 wt.% into Al film. Curvature measurement on the films provides useful information to illustrate the formation of hillocks and their inhibition. Very fine nano grains in 0.53 Sc film much smaller than those in other Al–Sc films offer the advantage of preventing the formation of hillocks. Al–0.53 wt.% Sc thin film is regarded as an excellent candidate for the reflector in new auto lamp with LED light source.

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