Uneven Crystallization of a-Si and a-Si: Ag Thin Films Irradiated by Femtosecond Laser

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Abstract. The crystallization of both a-Si and a-Si:Ag thin films by femtosecond laser irradiation has been studied recently. It is found that there is an uneven crystallization in both amorphous thin films by means of optical microscopy and laser Raman spectroscopy respectively. The crystallization in each pulse spot area is gradually weakened from the center to the edge along with the energy dispersion of laser irradiation. The laser induced crystallization in a-Si films begins early and develops more extensively compared to that in a-Si:Ag thin films, and Ag nanoparticles inhibits somehow the crystallization of a-Si in a-Si:Ag films.

1. Introduction

It is well known that amorphous silicon (a-Si) thin films are widely used in solar cells[1,2], optical modulators[3,4] and memristors[5,6], etc.. However, the Steabler-Wronski (S-W) effect [7,8] of a-Si is an inevitable problem in device fabrication. As a consequence, crystalline silicon thin film with high carrier mobility, wide spectrum absorption and non S-W effect becomes the focus. At present, there are many methods to fabricate crystalline silicon thin films, such as high temperature annealing crystallization [9], metal induced crystallization [12] and laser induced crystallization [10,11], etc., in which femtosecond laser induced crystallization of a-Si films [13] was concerned in the field of silicon-based microelectronic devices due to its good spatial selectivity and minimal thermal diffusivity. It is recently reported that Ag-doped a-Si (a-Si:Ag) thin film is used as a memristive dielectric material, realizing both switching and bio-synaptic functions[16]. Although there are many literatures[12,13,14] on femtosecond laser induced crystallization of purely a-Si materials, the study on femtosecond laser induced crystallization of Ag-doped a-Si (a-Si:Ag) thin film is rarely reported.

In our present study, the femtosecond laser induced crystallization of Ag-doped a-Si (a-Si:Ag) thin films have been investigated. The role of Ag nanoparticles in a-Si:Ag thin films is observed after the films are irradiated by femtosecond laser with different energies, and an uneven crystallization caused by femtosecond laser has been found both in a-Si:Ag thin films and a-Si thin films.

2. Experimental details

The a-Si:Ag and a-Si thin films were deposited on K9 substrates in a radio frequency (RF) co-sputtering system and the film thickness was kept about 300 nm. The chamber was pumped to a base pressure of...
7×10⁻⁴ Pa and the substrates were heated to 200°C before deposition. The RF power was set to 200 W. Argon (Ar) flow served as working gas was kept at 200 sccm to keep the chamber pressure in 0.5 Pa. To introduce Ag atoms, several Ag chips (99.99 %) were fixed on the Si target (99.999 %) and H2 flow was not introduced here. The nominal Ag concentration referring to 2.1 % and 4.9 % was estimated by the target coverage proportion of Ag chips and the sputtering yields.

A mode-locked Ti:sapphire laser (Solstice®) with parameters as 100 Hz, 800 nm and 80 fs was used to irradiate the a-Si:Ag and a-Si thin films. An optical microscope (MV5000) was used to observe the characteristics of irradiated spots resulted from femtosecond pulsed laser beam. Panalytical X’pert High Score XRD instrument was applied to measure the X-ray diffraction spectra, in which a conventional CuKα radiation (λ=1.5418 Å) was used, and the angle of incidence was set at 1°. The amorphous networks of both a-Si:Ag and a-Si thin films were analyzed by a RENISHAW inVia Raman Microscope at a wavelength of 514 nm. The power was set below 5 mW to avoid laser-induced crystallization. SEM observations were carried out using a JSM-7500F scanning electron microscope.

3. Results and discussion

Fig. 1(a) and 1(b) show the images of a-Si and a-Si:Ag films irradiated by femtosecond laser at the same conditions of 100 Hz beam frequency, 200 μm spot diameter, 15 mm/s scanning speed and 300 mJ/cm² beam energy density, respectively. It can be seen that each spot area from the center to the edge is gradually weakened as show in Fig 1(a) and 1(b) along with the energy dispersion of laser irradiation, which could be taken as a Gaussian type shown in Fig. 1(c). In this Gaussian model, the laser irradiation energy inside the center of the spot is the highest and is demonstrated as a red region. Apart from the red spot, the laser irradiation energy inside the orange ring area is relatively lower, and the irradiation energy outside the ring area is the lowest demonstrated as a gray base region. There exists an overlap area where the laser irradiation energy is a little bit higher than that in the gray base region.

Due to the fact that the energy distribution of fs laser beam is Gaussian[17,18], the laser induced crystallization of both a-Si and a-Si:Ag thin films differs from spot to spot even in a small area. Therefore, a chosen area can be divided into three parts: the center (zone I as in Fig. 2a), the ring (zone II as in Fig. 2b) and the outside (zone III as in Fig. 2c). Based on these divisions, Raman spectroscopy could be carried out to study the laser induced crystallization of both a-Si and a-Si:Ag thin films irradiated by femtosecond laser. Fig. 3 presents the variation of Raman spectra in different areas and in different films. Here, the a-Si thin films were irradiated at 100 mJ/cm² (Fig.3a) and the a-Si:Ag (2.1 % Ag) thin films were irradiated at 100 mJ/cm² (Fig.3b) or 300 mJ/cm² (Fig.3c), respectively. It can be seen that 100 mJ/cm² of fs laser energy density is sufficient to crystallize most part of the a-Si films (Fig.3a). For a-
Si:Ag films, however, large part of the films (Fig. 3b) is still noncrystallized, only the center of the spot appears the characteristic[19] of crystal silicon when irradiated at 100 mJ/cm². The irradiated spot as a whole of the a-Si:Ag films could be crystallized when the energy density is increased to 300 mJ/cm². The newly obtained experimental results demonstrate an uneven crystallization of a-Si:Ag films irradiated by femtosecond laser never published before. It is accepted that Ag nanoparticles in the a-Si:Ag films could absorb and scatter a large amount of irradiation energy, leading to a lower energy accumulating for the crystallization of a-Si:Ag films. Besides, owing to the nature of femtosecond laser beam[20], there is hardly heat flow inside the film during laser irradiation. Therefore, it is said hereby that Ag nanoparticles inhibits somehow the crystallization of a-Si in a-Si:Ag films.

Fig. 4 shows XRD spectra of a-Si and a-Si:Ag thin films irradiated at the same energy density of 300 mJ/cm². It can be seen that without Ag atoms, i.e. a-Si film has already been changed from amorphous state to almost crystallization state, because one can easily observe the peak of Si (111) located at 2θ=28.49° in Fig. 4. This situation has happened even at a lower irradiated energy density of 100 mJ/cm² as shown in Fig. 3a. This result means that the laser induced crystallization in a-Si films begins early and develops more extensively compared to that in a-Si:Ag thin films. The laser induced crystallization in a-Si:Ag thin films, however, is not so apparent. When the Ag content in a-Si:Ag films is increased from 2.1 % to 4.9 %, the peaks of Si (111), Si (220) and Si(331) gradually decreases and disappears. This means that Ag nanoparticles in the a-Si:Ag films DO inhibit the crystallization of a-Si. This XRD results are well coincided with Raman spectra mentioned above. Furthermore, one can hardly observe the so called metal-induced crystallization of in a-Si:Ag thin films. We know that there are not any Si-Ag binary crystals formed in the a-Si:Ag thin films, and that the femtosecond laser has a very short duration[20] of pulse action. During irradiation, the time taken in the pulse laser spot is so limited that there is not enough time to promote the crystallization progress taking Ag crystal as the nucleus of a-Si.
The femtosecond laser induced crystallization of a-Si and a-Si:Ag thin films can also be studied by SEM. Fig. 5(a) and 5(c) demonstrate the surface morphologies of a:Si and a-Si:Ag thin films irradiated at 300 mJ/cm². It can be seen from Fig. 5(a) that the polysilicon particles are relatively larger. The effect of laser induced crystallization of a-Si is obviously. In the situation of a-Si:Ag thin film, as can be seen from Fig. 5(b) that Ag nanoparticles distribute uniformly on the surface of the film before laser irradiation. The surface morphologies of the film is, however, apparently different from that of a-Si film after irradiated by femtosecond laser as shown in 5(a) and 5(c). Here, the effect of laser induced crystallization of a-Si:Ag is obviously inhibited.

4. Conclusion
In summary, the crystallization of both a-Si and a-Si:Ag thin films by femtosecond laser irradiation has been realized. An uneven crystallization is observed in both films through the studies of surface morphology and Raman spectroscopy. The crystallization in each pulse spot area is gradually weakened from the center to the edge along with the energy dispersion of laser irradiation, which is consistent with the Gaussian distribution. It is indicated that the femtosecond laser induced crystallization in a-Si films begins early and develops more extensively compared to that in a-Si:Ag thin films, and that Ag nanoparticles in the a-Si:Ag films could absorb and scatter a large amount of irradiation energy, resulting in a lower energy accumulating for the crystallization of a-Si:Ag films. Owing to the nature of femtosecond laser beam, there is hardly heat flow inside the amorphous thin films during laser irradiation, therefore, Ag nanoparticles inhibits somehow the crystallization of a-Si in a-Si:Ag films.

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