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BEHAVIOR OF HYDROGEN DURING CRYSTALLIZATION OF THIN SILICON FILMS DOPED WITH TIN

The behavior of a hydrogen impurity in the course of crystallization of thin silicon films doped with tin (a-SiSn films) has been studied. It is found that the band located at about 2000–2200 cm^{-1} and corresponding to the IR absorption at silicon–hydrogen bonds is absent from the spectra of as-deposited (at a temperature of 300 °C) a-SiSn films with Sn contents within the interval of 1–10 at.%. In undoped thin silicon films (a-Si films), the hydrogen content diminishes below the sensitivity threshold of the measurement technique only after the annealing of the specimens at 700 °C. The absence of hydrogen in a-SiSn films is in good agreement with the results of EPR studies and the results of Raman scattering studies of structural transformations in thermally treated films. It is shown that the formation of crystalline phases in a-SiSn occurs at lower temperatures as compared to those in a-Si, with a correlation taking place between the crystallization temperature for Si clusters and the concentration of the tin impurity. Taking into account that tin reduces the temperature of the hydrogen effusion from the film volume and, accordingly, stimulates the ordering in the specimen structure, it is possible to consider that hydrogen impurity takes part in the processes that result in a decrease of the crystallization temperature for a-SiSn.

Keywords: thin silicon films, crystallization, tin doping, hydrogen.

1. Introduction

The crystallization in thin silicon films doped with tin (a-SiSn films) is known [1–6] to start at temperatures that are lower in comparison with those for undoped thin silicon (a-Si) films. In particular, we demonstrated [1, 4] that the crystal phase with average crystallite dimensions smaller than 10 nm is formed in a-SiSn as early as in the course of film deposition onto a substrate at a temperature of 300 °C. This circumstance opens new opportunities for the fabrication of nanocrystalline silicon films at rather low temperatures. For this purpose, however, we need to understand the mechanism of crystal phase formation in a-SiSn films.

Hydrogen atoms, which are present in the film bulk just after the film has been grown or owing to the film hydrogenation, substantially affect the structural properties of a-Si. First, they passivate the dangling bonds of silicon; and, second, the hydrogen diffusion can stimulate the relaxation of stressed Si–Si bonds [7–10]. When a-Si films are annealed in the temperature interval 300–600 °C, hydrogen effuses from the film volume [3], and the film structure improves its ordering [11]. If the films are annealed at higher temperatures, the crystallization takes place in them [12, 13].

The doping of a-Si with various metal impurities, e.g., Ni, Al, Ag, Au, and Cu, is also known to result in a decrease of the silicon crystallization temperature [14]. Moreover, in accordance with the results of

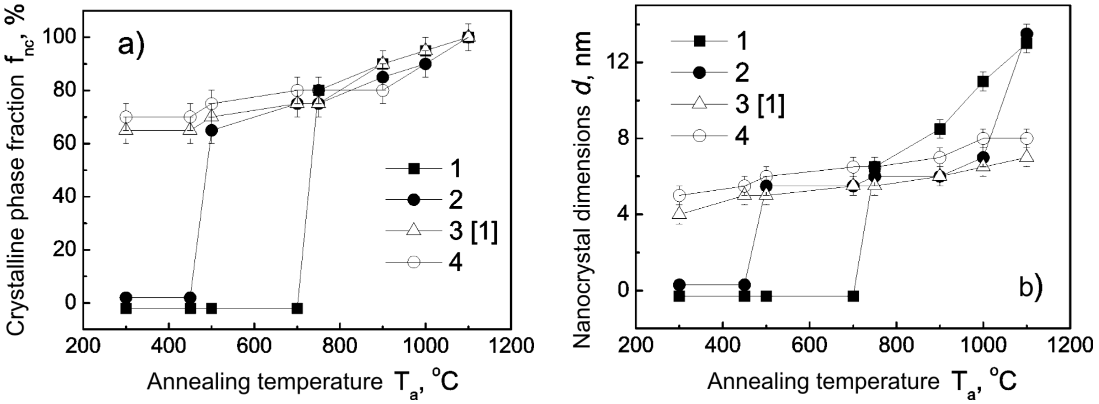

Fig. 1. Dependences of (*a*) the relative volume fraction of the silicon crystalline phase and (*b*) the nanocrystal dimensions in the films on the isochronous (for 20 min) annealing temperature: a-Si film (*1*), a-SiSn films with Sn contents of 1 (*2*), 4 (*3*), and 10 at.% (*4*). Spectrum *3* was obtained in work [1] and is shown for comparison

work [15], some metals have a catalytic effect on the silane decomposition. The authors of works [14, 16] supposed that a reduction of the a-Si:H crystallization temperature may probably be associated with the breaks of Si–H bonds induced by metal impurities at low temperatures.

The tin impurity also reduces the temperature of crystallization in amorphous silicon [1–6] and the temperature of hydrogen effusion [2, 3]. These facts mean that a decrease of the crystallization temperature for thin a-SiSn films can be associated with the hydrogen effusion induced by the tin impurity.

This work aimed at studying the behavior of hydrogen in the course of crystallization of thin silicon films doped with tin.

2. Experimental Part

In our researches, we used a-Si and a-SiSn films (in the latter case, the Sn content was about 1 or 10 at.%) obtained by thermally evaporating a Si powder and a mixture of Si and Sn powders, respectively, in a vacuum of about 10^{-3} Pa. The films were deposited onto silicon and quartz substrates at the temperature $T_s = 300$ °C. The film thickness was about 600 nm. The impurity content of the films was monitored using the Auger electron spectroscopy method on an Auger spectrometer JAMP-9500F.

To change the phase composition, the deposited films were isochronously annealed for $t_a = 20$ min in the argon atmosphere in the temperature interval from 300 to 1100 °C with a step of 50 °C. The phase composition of films was studied by analyzing the spectra of Raman light scattering. The Raman spectra were registered at room temperature on a spectrometer Jobin Yvon T-64000. The spectra were excited using the radiation emitted by an Ar^+ laser with a wavelength of 488 nm. By resolving the Raman spectra into the bands given by the amorphous and crystalline phases in the framework of the model of spatial confinement of phonons, we estimated the average dimensions of spherical crystallites, d, and the volume fraction of the crystalline phase, f_{nc}, for various annealing temperatures [17–19].

The concentration of hydrogen N_H in the a-Si films was determined from the optical absorption spectra in the IR region following the technique described in work [20],

$$N_\mathrm{H} = A_{2100} I_{2100},$$

where $A_{2100} = 2.2 \times 10^{20}$ cm^{-2}, $I_{2100} = \int \omega^{-1}\alpha(\omega)d\omega$ is the integral absorption intensity of the 2100-cm^{-1} mode, which corresponds to the hydrogen bonds in SiH$_x$ complexes ($x = 1, 2, ...$), and $\alpha(\omega)$ is the absorption coefficient [20–22]. The IR spectra were registered on a Fourier spectrometer Spectrum BXII Perkin Elmer at room temperature.

Defects in the deposited amorphous silicon films were studied using the electron paramagnetic resonance (EPR) method. The EPR spectra were registered at room temperature on an X-ray spectrometer (a microwave frequency of 9.4 GHz) with the magnetic field modulation at a frequency of 100 kHz. The number of defects was determined by comparing the double integrals of the first derivative of absorption

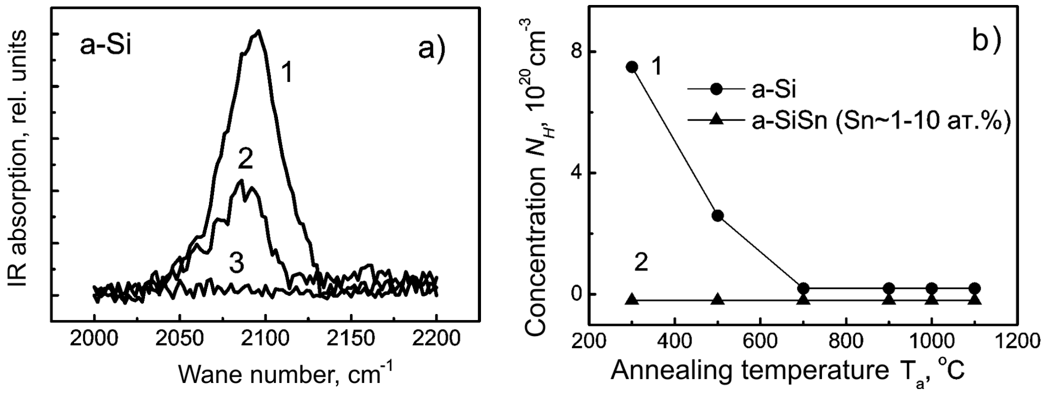

Fig. 2. (*a*) Spectra of optical density for thin a-Si films: as-deposited at $T_s = 300$ °C (*1*) and annealed at temperatures of 500 (*2*) and 700 °C (*3*). (*b*) Dependences of the hydrogen concentration in a-Si films (*1*) and a-SiSn films with Sn contents within the interval of 1–10 at.% (*2*) on the temperature of isochronous (for 20 min) annealing

signals obtained from either the examined specimen or the reference one (MgO:Mn^{2+}) with the known number of spins.

3. Results and Their Discussion

In Fig. 1, the dependences of the crystalline phase fraction (panel *a*) and the average crystallite dimensions (panel *b*) in the specimens, which were determined from the Raman spectra, on the isochronous annealing temperature in the interval 300–1100 °C are depicted. The dependences testify that the as-deposited a-Si and a-SiSn (about 1% Sn) films are amorphous. The analysis of the Raman spectra obtained for the structures of both types showed that silicon crystallites appear in a-SiSn at a lower annealing temperature in comparison with that for a-Si; namely, at 500 °C in a-SiSn ($f_{nc} \approx 65\%$, $d \approx 5.5$ nm) and at 750 °C in a-Si ($f_{nc} \approx 80\%$, $d \approx 6.5$ nm). The further annealing of the films of both types gives rise to the growth of the crystalline phase fraction and the crystallite dimensions in them. At $T_a = 1100$ °C, the specimens of both types become completely crystalline. Note that the average dimensions of silicon crystallites at the specimen annealing in the temperature interval of 750–1000 °C grow more rapidly in the undoped tin films. After the annealing at 1100 °C, the average dimensions of crystallites exceed 10 nm in the specimen of both types.

In contrast to the films discussed above, the structure of as-deposited a-SiSn specimens with the Sn content of about 10 at.% contained silicon nanocrystallites right after the deposition procedure. The size of those nanocrystallites was equal to about 5 nm, and their fraction to about 70%. The isochronous annealing results in a gradual growth of the parameters d and f_{nc}, so that, after the thermal treatment of the film at 1100 °C, $d \approx 8$ nm and $f_{nc} \approx 100\%$. It should be noted that the dependences of the average crystallite size and the crystal phase fraction on the isochronous annealing temperature obtained for a-SiSn films with about 10 at.% of Sn turned out almost the same as for a-SiSn films with about 4 at.% of Sn (curve 4 in Fig. 1), which were studied in work [1].

Together with the phase composition of the films, we also analyzed the behavior of hydrogen at thermal treatments. It turned out that the band corresponding to the absorption at silicon–hydrogen bonds (a frequency interval of 2000–2200 cm^{-1}) was not observed in as-deposited a-SiSn films, in contrast to a-Si ones. In Fig. 2,*a*, the optical density spectra for thin a-Si films annealed at various temperatures are shown, and Fig. 2,*b* demonstrates the variation of hydrogen concentrations in a-Si and a-SiSn films as functions of the annealing temperature. One can see that the hydrogen concentration in the as-deposited a-Si specimens amounted to about 7.5×10^{20} cm^{-3}. As the temperature of thermal treatment increased, the absorption intensity in the band at about 2100 cm^{-1} decreased for a-Si and disappeared altogether after the annealing at 700 °C, which testifies to the hydrogen effusion from the film volume (Fig. 2). Afterward, the process of a-Si crystallization began (Fig. 1). The concentration of Si–H$_x$ bonds in a-SiSn was lower than the sensitivity threshold of the research method in the whole interval of annealing temperatures. Note that no ab-

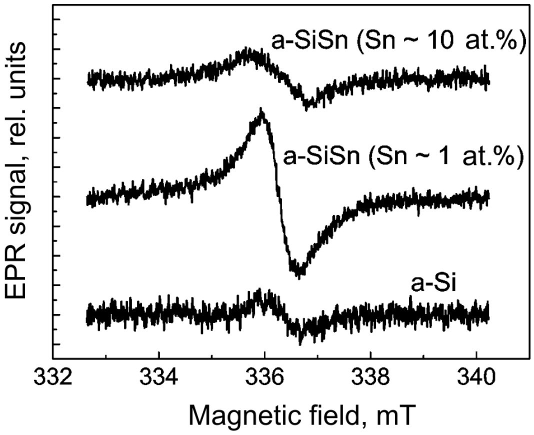

Fig. 3. EPR spectra for as-deposited a-Si and a-SiSn films registered under identical conditions

sorption at Sn–H bonds was observed for the silicon films doped with tin, because hydrogen atoms predominantly form bonds with silicon rather than tin ones [2, 3, 23]. Therefore, we may consider hydrogen to be absent from the structure of a-SiSn specimens studied in this work.

Since hydrogen atoms passivate dangling bonds in the bulk of amorphous silicon films, and those bonds are paramagnetic centers, the hydrogen effusion from the a-Si structure and the hydrogen absence from a-SiSn may manifest themselves in the results of EPR researches. In Fig. 3, the EPR spectra of as-deposited a-Si and a-SiSn films are shown. All spectra include a wide line with a g-factor equal to 2.0051 ± 0.0002, which is typical of dangling silicon bonds in a-Si [24]. The concentration of paramagnetic defects determined from the EPR spectra assuming their uniform distribution across the film thickness amounts to 1.1×10^{18} cm^{-3} for the a-Si specimen, 6.0×10^{18} cm^{-3} for the a-SiSn specimen with a Sn content of about 1 at.%, and 1.6×10^{18} cm^{-3} for the a-SiSn specimen with a Sn content of about 10 at.%. These data agree well with the results of IR absorption researches and the obtained temperature dependences for the parameters d and f_{nc}. In particular, the as-deposited a-Si and a-SiSn (1 at.% Sn) films have an amorphous structure, but the number of dangling bonds in the a-Si film is much smaller owing to their passivation by hydrogen. In the a-SiSn specimens with a Sn content of about 10 at.%, hydrogen is absent; but owing to a higher structural perfection of specimens (the crystalline phase fraction $f_{nc} \approx 70$ vol.%), the EPR signal is somewhat stronger than that for a-Si, but considerably lower than that in the case of a-SiSn with a Sn content of about 1 at.%.

The presence of tin is known to weaken the Si–H bonds [23], so that the hydrogen effusion begins at lower temperatures [3, 23]. It should be noted that tin can accelerate the oxygen diffusion in single-crystalline silicon [25]. Therefore, on the basis of experimental data, we suppose that the lowering of the a-SiSn crystallization temperature is associated with the breaks of Si–H bonds induced by tin at low temperatures, which is accompanied by the hydrogen effusion from the silicon film and the subsequent crystallization of amorphous silicon. Accordingly, we consider the hydrogen effusion and the silicon crystallization as two interconnected and complementary processes giving rise to the crystallization of amorphous silicon. The higher the hydrogen or tin concentration in such specimens, the more effective is the crystallization of amorphous silicon.

In particular, in the case where silicon is doped with tin to about 1 at.% (this concentration is, most likely, a bit higher than the tin solubility concentration in amorphous silicon), the majority of tin atoms become uniformly distributed in the silicon specimen. The number of regions with an enhanced tin content is small; moreover, their sizes are also small. At a temperature of 300 °C, at which hydrogen effuses from the silicon film, nuclei of the crystalline phase can be formed in the a-SiSn specimens with a Sn content of 1 at.%. However, their concentration (the crystalline phase fraction) is too low, and their sizes are too small for the modifications in the structure of examined specimens to be registered with the help of our measurement techniques. The fact that the crystalline phase can already be detected at a temperature of 500 °C testifies in favor of the assumption that nuclei of the crystalline phase are formed in the a-SiSn specimens with a Sn content of 1 at.% at 300 °C. If those nuclei of the silicon crystalline phase were absent, this temperature would have been considerably higher.

At tin-doping levels of about 4 and 10 at.%, the crystallization in the specimens at their thermal treatments occurs identically (the specific saturation at a given temperature takes place), and an amorphous-crystalline structure with crystallite dimensions of about 5 nm is formed during the film growth process.

Note that, in a-SiSn films, the crystal phase is composed of crystallites with the average dimensions less than 10 nm in a wide temperature interval. At the same time, crystallites in undoped films rapidly grow with increase of the thermal treatment temperature to dimensions exceeding 10 nm. The explanation of this fact needs additional researches. We may suppose that the tin impurity not only affects the hydrogen effusion and the silicon crystallization, but also confines the dimensions of silicon crystallites.

4. Conclusions

While studying the behavior of hydrogen in the course of crystallization of thin a-SiSn films with Sn contents within the interval 1–10 at.%, the following facts were established.

– The crystal phase in a-SiSn is formed at a lower temperature than that in a-Si. A correlation between the crystallization temperature of Si clusters and the tin impurity concentration is observed. More specifically, the formation of an amorphous-crystalline structure begins in the course of deposition onto a substrate at 750 °C in a-Si, at 500 °C in a-SiSn with a Sn content of about 1 at.% and at 300 °C in a-SiSn with a Sn content within the interval 4–10 at.%.

– In the spectra of as-deposited a-SiSn films, the band at 2000–2200 cm^{-1} corresponding to the IR absorption at silicon–hydrogen bonds is absent, in contrast to those of a-Si films, from which hydrogen completely effuses only after the film is annealed at a temperature of 700 °C. This fact agrees well with the results of EPR researches and the structural (phase) transformations of films observed at their thermal treatment.

– Taking into account that tin reduces the temperature of the hydrogen effusion from the film volume and, accordingly, stimulates the ordering in the specimen structure, it is possible to consider that the hydrogen impurity takes part in the processes that result in a decrease of the crystallization temperature for a-SiSn.

– Silicon nanocrystallites in a-SiSn have an average size smaller than 10 nm in a wide temperature interval of thermal treatments. At the same time, crystallites in a-Si rapidly grow with the annealing temperature and become larger than 10 nm in dimensions. This fact may testify that the tin impurity confines the growth of silicon nanocrystallites.

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ПОВЕДІНКА ВОДНЮ ПРИ КРИСТАЛІЗАЦІЇ ТОНКИХ ПЛІВОК КРЕМНІЮ, ЛЕГОВАНИХ ОЛОВОМ

Резюме

Досліджено поведінку домішки водню під час кристалізації тонких плівок кремнію, легованих оловом (a-SiSn). Встановлено, що у плівках a-SiSn (вміст Sn ∼ 1–10 ат.%) безпосередньо після осадження (300 °C) відсутня смуга ІЧ поглинання на кремній-водневих зв'язках (область ∼2000–2200 см$^{-1}$). У нелегованому a-Si вміст водню стає меншим межі чутливості даної методики дослідження лише після відпалу при 700 °C. Факт відсутності водню у a-SiSn добре узгоджується з ЕПР дослідженнями та структурними перетвореннями плівок при термообробках, які досліджувалися методом комбінаційного розсіяння світла. Показано, що формування кристалічної фази у a-SiSn відбувається при нижчих температурах порівняно з a-Si. При цьому спостерігається кореляція між температурою кристалізації Si кластерів та концентрацією домішки олова. Враховуючи те, що олово зменшує температуру ефузії водню з об'єму плівок і, відповідно, стимулює впорядкування структури зразків, можна припустити, що домішка водню бере участь в процесах, що ведуть до зниження температури кристалізації a-SiSn.