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INFLUENCE OF HIGH TEMPERATURE ANNEALING ON THE STRUCTURE AND THE INTRINSIC ABSORPTION EDGE OF THIN-FILM SILICON DOPED WITH TIN

Influence of isochronal annealing in the range of 350–1100 ℃ on the structural properties and the intrinsic absorption edge in thin silicon films doped with tin (a-SiSn) has been studied. It is found that as-deposited a-SiSn films with a tin content of about 4 at.%, unlike undoped a-Si ones, contain silicon nanocrystals with a crystallite size of about 4 nm and a crystalline fraction of about 65%. It is shown that, in the course of isochronal annealing of a-SiSn specimens in the interval of 350–1100 ℃, the size of silicon nanocrystals in the amorphous matrix gradually increases to about 7 nm, and the fraction of crystalline phase to about 100%. Crystallization in undoped a-Si is observed only after the annealing at temperatures above 700 ℃. The influence of tin on the optical band gap in a-Si as a function of the isochronal annealing temperature is analyzed.

Keywords: thin-film silicon, doping with tin, crystallization, optical band gap, isochronal annealing.

1. Introduction

Thin-film silicon is a promising material for optoelectronic devices, including solar cells. Especially challenging are two-phase amorphous-crystalline silicon structures possessing a higher stability of its parameters to the action of light [1, 2]. An important task is the development of technologies aimed at the fabrication of thin amorphous-crystalline silicon films with required properties, when the crystallization temperature is relatively low.

It is known [3–6] that the doping of silicon films with metal impurities – Al, Au, Ni, and others z – allows the temperature of film crystallization to be lowered. In work [7], we found experimentally that the tin doping also results in the formation of a nanocrystalline phase in the amorphous silicon matrix, with this process occurring in the course of silicon deposition onto the substrate at a temperature of 300 °C.

Thermal treatment is another way to affect the properties of thin-film silicon. It is known [1, 8] that the annealing at temperatures above 350 °C induces substantial changes in the properties of formed amorphous silicon films. Therefore, in order to optimize the technology of synthesis of amorphous-crystalline silicon films–in particular, doped with tin–it is necessary that the processes that run in the films at elevated temperatures should be studied in detail. This work aimed at researching the influence of the high-temperature isochronous annealing on the structural properties and the intrinsic absorption edge of thin tin-doped silicon films.

2. Experimental Part

Two batches of specimens were fabricated either by thermally evaporating the single-crystalline Si powder (batch I) or a mixture of single-crystalline Si and Sn powders (batch II). The films were grown in a vacuum of about 10^{-3} Pa on silicon and quartz substrates at the temperature $T_s = 300$ °C. The film thickness was 200–600 nm. The impurity com-

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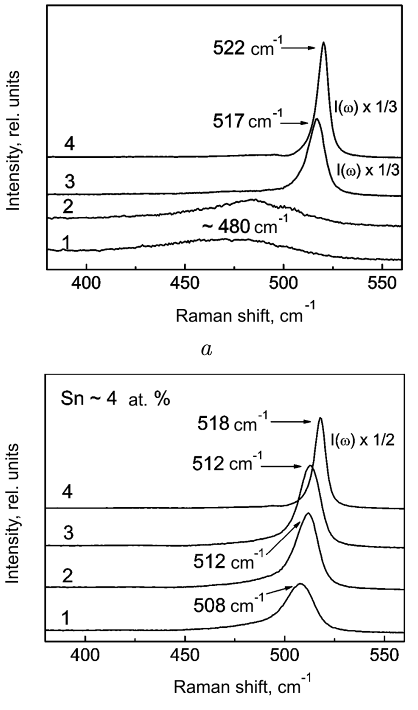

a

b

Fig. 1. Raman spectra obtained for as-deposited specimens (*1*) in batches I (*a*) and II (*b*) and after the isochronous annealing at 700 (*2*), 750 (*3*), and 1100 °C (*4*)

position of the films was monitored with the use of Auger-electron spectroscopy (an Auger-spectrometer JAMP-9500F). In the films of batch II, the Sn content amounted to about 4 at.%.

To study the influence of a thermal treatment on the structural and optical properties of formed films, the specimens from both batches were subjected to the isochronous annealing for $t_a = 20$ min in an argon environment and in the temperature interval from 350 to 1100° with an increment of 50 °C. Information on the structure and the phase composition of studied films was obtained by analyzing the Raman scattering spectra, which were registered at room temperature. For the spectrum excitation, an Ar$^+$-laser with a wavelength of 488 nm was used. The intrinsic absorption edge was studied by measuring the transmission spectra of specimens in the interval of 1.4–2.8 eV on a SHIMADZU UV-2450 spectrophotometer.

3. Results and Their Discussion

In Fig. 1, the Raman spectra of specimens from batches I and II obtained after the deposition and the following isochronous annealing are shown. Undoped films, both as-sputtered (Fig. 1, *a*, curve *1*) and after the isochronous annealing at a temperature of 700 °C (Fig. 1, *a*, curve *2*), have an amorphous structure, which is evidenced by a wide band in their spectra with a maximum in a vicinity of 480 cm^{-1} [9–11]. Annealing at $T_a = 750$ °C gives rise to the appearance of a narrow small peak with a maximum at about 517 cm^{-1} (Fig. 1, *a*, curve *3*), which demonstrates the presence of the crystalline silicon phase in the structure of *a*-Si specimens [9–11]. After the following annealing at higher temperatures, the peak position shifts toward high frequencies up to 522 cm^{-1} (Fig. 1, *a*, curve *4*), and the band intensity drastically increases. This peak position is typical of crystalline silicon [9–11].

In tin-doped silicon films (*a*-SiSn), unlike undoped ones (*a*-Si), silicon nanocrystals were observed already in the structure of as-deposited films (a small peak at about 508 cm^{-1} (Fig. 1, *b*, curve *1*)). As the temperature of the isochronous annealing increased, the intensity of this peak gradually grew, and the peak itself shifted into the high-frequency region. After the annealing at 1100 °C, the peak maximum was observed at about 518 cm^{-1} (Fig. 1, *b*, curve *4*).

With the help of the phonon confinement model [9–11], we analyzed the experimental Raman spectra in order to determine the influence of the isochronous annealing temperature on the volume fraction of the crystalline silicon phase, f_{nc}, and the size of crystallites, d, in the *a*-Si and *a*-SiSn films. The obtained values for the structural parameters d and f_{nc} are quoted in Table. One can see that the structure of as-deposited *a*-SiSn films contains crystallites about 4 nm in dimensions, and their volume fraction amounts to 65%. Isochronous annealing of *a*-SiSn films in the interval of 350–1100 °C allows the dimensions of nanocrystals in the amorphous matrix to grow gradually from 4 to about 7 nm. The volume fraction of the crystal phase grows at that from 65 to 100%.

At the same time, the crystallization in undoped *a*-Si films began only if the annealing temperature was higher than 700 °C. After the thermal treatment at 750 °C, approximately 80% of the film volume were occupied by the crystalline phase with crystallite dimensions of about 6.5 nm (see Table). An increase of the isochronous annealing temperature gave rise to a quick growth of the crystalline phase fraction and the crystallite dimensions. In particular, after the annealing at 1100 °C, $f_{nc} \approx 100\%$ and $d > 10$ nm.

The optical band gap, E_g, in amorphous-crystalline silicon films can be determined with the help of the Tauc relation, $\alpha(h\nu)h\nu = B(h\nu - E_g)^2$, where α is the coefficient of optical absorption, and B the proportionality factor [12–14]. For this purpose, the absorption spectra are plotted in the coordinates $(\alpha h\nu)^{1/2}$ versus $h\nu$. The extrapolation of the linear section in the spectrum to zero gives the E_g-value. In Fig. 2, the spectral dependences of the quantity $(\alpha h\nu)^{1/2}$ versus $h\nu$ are shown for the initial *a*-Si and *a*-SiSn specimens ($T_s = 300$ °C) and the specimens annealed at $T_a = 1100$ °C. We see that the linear sections in the spectra of initial specimens extend within the interval 2 eV $\leq h\nu \leq$ 2.8 eV, whereas, for the annealed specimens, the linear section becomes shorter and shifted toward lower energies, 1.8 eV $\leq h\nu \leq$ 2.3 eV. The values obtained for E_g are listed in Table.

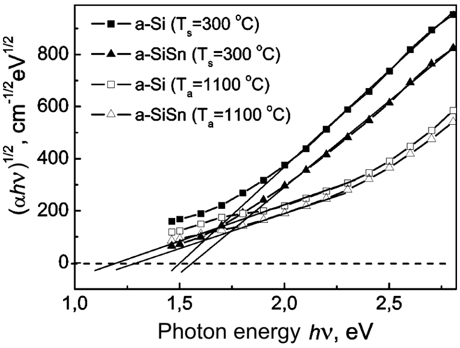

Fig. 2. Spectra of optical absorption in the initial *a*-Si and *a*-SiSn specimens ($T_s = 300$ °C) and annealed $T_a = 1100$ °C. Extrapolation of the linear section to zero gives the value of E_g

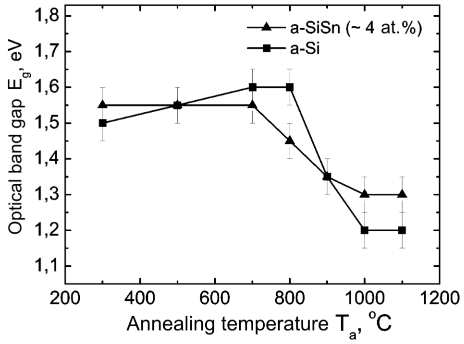

Fig. 3. Dependences of the optical energy gap width in *a*-Si and *a*-SiSn films on the isochronous (20 min) annealing temperature

Figure 3 demonstrates the dependences of the optical band gap in the *a*-Si and *a*-SiSn films on the isochronous annealing temperature. One can see that, in the as-deposited *a*-SiSn films, $E_g \approx 1.55$ eV and does not change at the isochronous annealing at $T_a < < 700$ °C. In the as-deposited *a*-Si films, $E_g \approx \approx 1.50$ eV. At the isochronous annealing at $T_a < 800$ °C, a small increase of E_g to 1.60 eV is observed, which, according to work [15], can be associated with a reduction of internal stresses owing to the structure ordering. After the annealing of *a*-Si specimens at temperatures higher than 800 °C, the magnitude of E_g gradually decreases to attain a value of about 1.2 eV at $T_a = 1100$ °C, which is close to the optical band gap in crystalline silicon at room temperature (1.12 eV). In *a*-SiSn specimens, the value of E_g starts to diminish at temperatures higher than 700 °C, and, after the annealing at 1100 °C, reaches the value $E_g \approx 1.3$ eV.

Structural and optical parameters of examined specimens

Specimens	T °C	$d \pm 0.5$, nm	$f_{nc} \pm 5$, %	$E_g \pm 0.05$, eV
a-Si	300	0	0	1.5
	500	0	0	1.55
	700	0	0	1.6
	750	6.5	80	1.6
	800	7.0	85	1.6
	900	8.5	90	1.35
	1000	11.0	95	1.2
	1100	13.0	100	1.2
a-SiSn	300	4.0	65	1.55
	500	5	70	1.55
	700	5.5	75	1.55
	750	5.5	75	1.5
	800	5.5	80	1.45
	900	6.0	90	1.35
	1000	6.5	95	1.3
	1100	7.0	100	1.3

As was shown above, the structure of tin-doped films after the annealing at 1100 °C is completely crystalline, with the average size of crystallites being about 7 nm, and $E_g \approx 1.3$ eV. These results agree well with the results of theoretical calculations in work [16], where the optical band gap in silicon nanocrystals 7 nm in diameter was calculated to be equal to about 1.35 eV.

4. Conclusions

While studying the influence of the isochronous annealing in the temperature interval of 350–1100 °C on the structural properties and the intrinsic absorption edge of thin *a*-SiSn films, the following results were obtained.

– The structure of as-deposited *a*-SiSn specimens (a tin content of about 4 at.%), unlike that of undoped *a*-Si ones, contains silicon nano-crystals. The size of crystallites is about 6 nm, and the fraction of the crystalline phase amounts to about 65%.

– Isochronous annealing of *a*-SiSn specimens at $T_a = 350 \div 1100$ °C gradually increases the average size of silicon nano-crystals in the amorphous matrix to about 7 nm, and the crystalline phase fraction to about 100%. Crystallization in undoped *a*-Si specimens begins only at annealing temperatures higher than 700 °C. At $T_a = 1100$ °C, the structure becomes completely crystalline, with the crystallite dimensions exceeding 10 nm.

– In the as-sputtered specimens, the optical band gap amounts to about 1.55 (*a*-SiSn) and 1.5 eV (*a*-Si).

– After the annealing of *a*-Si specimens at temperatures higher than 800 °C and *a*-SiSn specimens at temperatures higher than 700 °C, the optical band gap gradually decreases to about 1.2 and 1.3 eV, respectively (at $T_a = 1100$ °C).

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ВПЛИВ ВИСОКОТЕМПЕРАТУРНОГО ВІДПАЛУ НА СТРУКТУРУ ТА КРАЙ ВЛАСНОГО ПОГЛИНАННЯ ТОНКОПЛІВКОВОГО КРЕМНІЮ, ЛЕГОВАНОГО ОЛОВОМ

Резюме

Досліджено вплив ізохронного відпалу в діапазоні 350–1100 °C на структурні властивості та край власного поглинання тонких плівок кремнію, легованих оловом (*a*-SiSn). Отримано, що у структурі *a*-SiSn (олова ∼4 ат. %), на відміну від нелегованого *a*-Si, зразу після осадження присутні нанокристали кремнію (розмір кристалітів ∼4 нм, частка кристалічної фази ∼65%). Показано, що ізохронний відпал *a*-SiSn в діапазоні 350–1100 °C поступово збільшує розміри нанокристалів кремнію в аморфній матриці до ∼7 нм, а частку кристалічної фази до ∼100%. Кристалізація нелегованого оловом *a*-Si починається лише при температурах відпалу більше 700 °C. Проаналізовано вплив олова на оптичну ширину забороненої зони *a*-Si залежно від температури ізохронного відпалу.