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The influence of deposition parameters on the structure of nanocrystalline silicon

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Abstract. Nanocrystalline silicon films have been produced by PECVD method in $SiH_4 + H_2$ gas mixtures. Raman spectra, IR absorption and absorption edge of the films have been investigated in a function of such deposition parameters as the gas dilution ratio, H_2O contamination, the deposition temperature (T_s) and the material of the substrate. The study of IR spectra has showed the presence of bonded hydrogen, with the total concentration (C_H) varying from 4 to 13 at.%. The analysis of Raman spectra has revealed that the films contain nanocrystallites embedded in amorphous matrix. The size of crystallite (R) has been evaluated from the shift of the peak in Raman spectra corresponding to crystalline phase and has been found to be in a range 38–57 Å. The volume fraction of crystallites (X_c), which varied from 15% to 81%, has been estimated from the intensity of this peak. Both values, X_c and R, are primarily influenced by H_2O contamination, while the effect of T_s is less pronounced. The size of crystallites displays also a strong dependence of the substrate material. IR investigations show that at $T_s = 160°C$ amorphous matrix contains polymeric phase which disappears at $T_s = 340°C$.

Introduction

The intensive investigations of silicon films containing nanocrystals was stimulated by the discovery in 1990 by L. T. Canham [ ] of photoluminescence in visible region at room temperature in porous silicon. This phenomenon implied the possibility of creation of silicon based photoelectronic devices. Further investigations have revealed that the intensity and wavelength of photoluminescence are closely connected with the size (R) and volume fraction of nanocrystals (X_c) [ ]. When produced by other methods, the silicon films consist of mixtures, where nanocrystals and microcrystals are embedded in amorphous phase. At low X_c amorphous phase plays a role of a bounding tissue while at high X_c it becomes just an interface between crystals. Thus, one of the urgent technological problems is how to control the size of and the concentration of nano- and microcrystals.

In present work we demonstrate the results of our investigations concerning optical properties of silicon films produced by Plasma Enhanced Chemical Vapor Deposition (PECVD) and show that these films contain a large fraction of nano- and microcrystallites included in amorphous tissue. We show also that the concentration and the size of crystallites may be effectively changed by variation of deposition parameters.

1 Experimental techniques

The nc-Si:H films were prepared by PECVD method. The mixture of $SiH_4 + H_2$ was used as the initial gas. The dilution ratio (SiH_4/H_2) was varied from 0.5 to 1.5. In some experiments the initial gas was contaminated by H_2O. The quartz and silicon single crystals were used

as the substrates and the deposition temperature (T_s) was varied from 160 to 340°C. The deposition parameters are summarized in the Table 1.

The films structure was investigated by Raman spectroscopy. The spectra were measured in automated installation based on DFS-24 spectrometer. The definition was not less than 3 cm^{-1}. The excitation was done by Ar^+ laser at wavelength 4880 Å. The measurements were carried out at minimum intensity to avoid the heating of the sample. The method of R and X_c calculation from Raman spectra is described in details in [ ].

IR spectroscopy was used for the determination of hydrogen concentration (C_H) and bonding configurations. C_H was determined from integrated absorption at 630 cm^{-1} (for oxygen free samples) or 2090 cm^{-1} (for samples contaminated by oxygen).

Optical gap was determined from optical transmission measurements and was calculated from Tauc plot [ ]: $\sqrt{\alpha h\nu} = f(h\nu)$.

2 Results and discussion

2.1 The influence of the initial gas dilution by hydrogen on the films structure

In this section we discuss the changes in nc-Si:H films structure caused by the dilution of initial gas by hydrogen. Figure 1 displays Raman spectra of PECVD nc-Si:H corresponding to TO-phonon absorption. It can be clearly seen that the spectrum consists of two lines with substantially different width. The broad line may be associated with the amorphous phase and is centered at about 480 cm^{-1}. The narrow one is situated at approximately 517.5 cm^{-1} and reflects the presence of crystalline phase. The interpretation of Raman

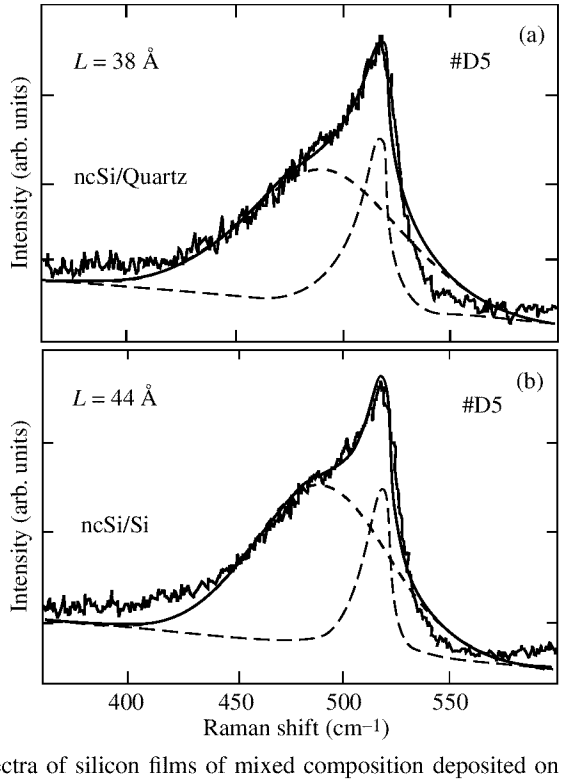

Fig. 1. Raman spectra of silicon films of mixed composition deposited on different substrates. (a) quartz. (b) c–Si.

Table 1. Deposition parameters and characteristics of nanosilicon films.

		Samples					
		D1	D2	D3	D4	D5	D6
Dilution ratio	SiH_4/H_2	1.5	1.0	0.5	0.5	0.5	0.5
Deposition temperature	T_s, °C	160	160	160	160	340	340
Thickness	d, μm	1.3	0.95	0.85	0.85	0.52	0.48
Deposition rate	v, Å/s	0.80	0.58	0.35	0.37	0.28	0.21
Size of nanocrystals on quartz	R, Å	49	50	57	38	44	54
Volume fraction of nc on quartz	X_c	0.78	0.75	0.74	0.15	0.50	0.81
Size of nanocrystals on c–Si	R, Å	40	37	49	36	38	49
Volume fraction of nc on c–Si	X_c	0.78	0.80	0.76	0.40	0.56	0.82
Hydrogen concentration	C_H at%	4.8	6.7	9.0	13.0	4.1	2.8
Oxygen concentration	C_O at%	—	—	—	0.4	1.4	—
Optical gap	E_g^{opt}, eV	—	1.94	—	—	—	1.74

spectra in accordance with the method developed in [3] allowed us to evaluate the size of nanocrystals (R) and their volume fraction (X_c). Our data show that the dilution of SiH_4 by H_2 leads to increase of R from 49 to 57 Å, while X_c remains approximately unchanged ~ 0.7. IR investigations reveal that the amorphous phase consists of silicon bonded with hydrogen in monomer Si–H and polymer $(Si{-}H_2)_n$ configurations. The gas dilution by hydrogen leads to further polymerization what corresponds to the increase of absorption coefficient at $\sim 2090\,cm^{-1}$ and $\sim 890\,cm^{-1}$.

2.2 The influence of deposition temperature

At permanent deposition condition the T_s increase from 160°C to 340°C influences the nanocrystallites very slightly. X_c varies from 0.74 to 0.81 and R from 57 to 54 Å. But the subsequent changes of amorphous phase are much greater. The T_s growth leads to disappearing of polymer chains, what is detected as the absence of IR absorption at 800–900 cm^{-1}. At greater T_s H is distributed on crystal grains in Si–H form.

2.3 The influence of H_2O contamination

In accordance with our experiments the greatest changes of nanocrystal phase were caused by the presence of H_2O vapour in initial gas what leads to substitution of hydrogen atoms by O–H groups. As can be seen in Table 1 R may be varied by this method from 57 to 38 Å with simultaneous change of X_c from 0.74 to 0.15. The amorphous phase is also remarkably reconstructed: the total concentration of H is increased, and as a considerable amount of the oxygen enters in the network in Si–O–Si form, what leads to growth of the absorption at 1080 cm^{-1}.

2.4 The influence of substrate material

To understand the role of substrate material in nanocrystals formation the films were deposited on quart and silicon single crystal (c–Si). The Table 1 illustrates that on the c–Si the size of nanocrystals is $\sim 6{-}10$ Å greater than on the quartz, while their concentration remains nearly the same. It may be explained in the following way. The initial concentration of nanocrystals seems to be equal for both substrates but their following growth is faster on c–Si substrate due to higher thermal conductivity of c–Si and hence higher mobility of radicals participating in the growth of nanocrystals.

3 Conclusions

In accordance with our results we can conclude:
— PECVD method permits to produce the silicon films of mixed composition with characteristic size of nanocrystallites ranging from $\sim$ 30 to $\sim$ 60 Å by use of $SiH_4 + H_2$ gas mixtures.
— The size of nanocrystallites, the structure of amorphous phase and the film growth rate may be varied by the dilution of silane by hydrogen.
— The structure of amorphous phase is much more sensitive to deposition temperature than that of crystalline phase.
— The size and the concentration of nanocrystallites are two times less in the films produced from silane contaminated by H_2O.
— The size of nanocrystallites on c–Si substrates is greater than on quartz substrates.

Acknowledgments

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References

[1] L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
[2] S. Tong, X. Lin, L. Wang, F. Yan and X. Bao, *Appl. Phys. Lett.* **69**, 596 (1996).
[3] V. G. Golubev, V. Yu. Davydov, A. V. Medvedev, A. B. Pevtsov and N. A. Feoktistov, *Phys. Solid State* **39**, 11197 (1997).
[4] J. Tauc, *Optical Properties of Amorphous Semiconductors* in *Amorphous and Liquid Semiconductors*, Plenum Press, London and New York (1974), p. 159.