Structure features of protocrystalline silicon films

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***Abstract* — The structural and electronic properties of thin protocrystalline silicon films obtained by plasma-enhanced chemical vapor deposition from hydrogen (H_2) and monosilane (SiH_4) gas mixture have been studied by means of transmission electron microscopy, electron paramagnetic resonance (EPR) spectroscopy, and Raman spectroscopy. It has been established that the studied films consist of the amorphous phase containing silicon nanocrystalline inclusions with the average size on the order of 4–5 nm and the volume fraction of 10%. The EPR spectroscopy data show that in the investigated samples there are electrons trapped in the conduction band tail of protocrystalline silicon. It has been shown that the introduction of a small fraction of nanocrystals into the amorphous silicon films nonadditively changes the electronic properties of the material.**

***Index Terms* — protocrystalline silicon films, TEM, EPR, Raman spectroscopy.**

I. INTRODUCTION

Recent investigations [1, 2] indicate that protoctystalline silicon films (pc-Si:H)—a material being a silicon amorphous matrix with a small fraction (not more than 10–15%) of nanocrystalline inclusions—has better electrical properties and higher stability of the electrophysical parameters to photo-degradation than hydrogenated amorphous silicon (a-Si:H). It was assumed that the presence of silicon nanocrystals (nc-Si) in the structure improves the order in the location of the atoms in the material, leading to an increase in the mobility of the charge carriers and the length of their ambipolar diffusion [2, 3] and to a considerable decrease in the density of defect states in the mobility gap [4]. To understand the non-equilibrium electron processes in pc-Si:H films and their application, in particular, in photoelectrical converters, it is necessary to study the electronic and structural properties of this material. In present work the complex of transmission electron microscopy (TEM), Raman spectroscopy, and electron paramagnetic resonance (EPR) spectroscopy was used to study this problem .

II. EXPERIMENTAL DETAILS

The pc-Si:H films with a thickness of 0.3 μm were obtained by plasma-enhanced chemical vapor deposition from the mixture of hydrogen (H_2) and monosilane (SiH_4) gases on a quartz substrate at a temperature of 275°C. The volume ratio of the gases in the reaction chamber was $R_H=[H_2]/[SiH_4] = 5$. The pressure in it was kept at the level of 4990 mTorr. The film deposition rate was 11 Å/s. To determine the role of nanocrystals in the pc-Si:H films, the obtained results were compared with the results of the measurements for a-Si:H films, that were formed by plasma enhanced chemical vapor deposition. The deposition parameters of the a-Si:H films were as follows: thickness, 0.5 μm; RH = 0; substrate temperature, 175°C; deposition rate, 0.7 Å/s.

The films were studied using a JEM-2100F transmission electron microscope (JEOL) at an accelerating voltage of 200 kV. Raman spectra were measured with a LabRam HR800 Horiba Jobin Yvon micro-Raman spectrometer at an excitation radiation wavelength of 488 nm in the backscattering geometry. Electron paramagnetic resonance spectra were recorded by an ELEXSYS_500 EPR spectrometer (Bruker) with a working frequency of 9.5 GHz and a sensitivity of $5 \cdot 10^{10}$ spin/G.

III. RESULTS AND DISSCUSSION

The TEM data shows that the structure of the pc-Si:H films was an amorphous silicon matrix with embedded silicon nanocrystals. The size distribution of silicon nanocrystals was obtained from the analysis of the photomicrographs taken at different places of the pc-Si:H film, and the average diameter of nanocrystals in the sample was $d = 4.2 \pm 1.0$ nm.

The volume fraction of the crystalline phase in the pc-Si:H samples was determined from the analysis of the Raman spectrum. The obtained spectrum were approximated by using the maxima characteristic of hydrogenated silicon films with two phase structure. The maxima near the frequencies $\omega_{LA} = 310$ cm^{-1} and $\omega_{LO} = 410$ cm^{-1} were attributed to the longitudinal acoustic (LA) and longitudinal optical (LO) phonon modes, respectively, in a-Si:H [5]. The maximum near the frequency $\omega_A = 480$ cm^{-1} corresponded to the transverse

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optical (TO) phonon mode in the amorphous structure of silicon [6]. The maximum near the frequency $\omega_C = 520$ cm^{-1} corresponded to the TO phonons of the crystalline silicon [7]. The maximum near the frequency $\omega_I = 500$ cm^{-1} was related to the transverse optical phonons. It is called the intermediary one because it is located between the maxima corresponding to the amorphous and crystalline structures. The interpretation of this band is still under discussion.

The volume fraction of the nanocrystalline phase in the studied pc-Si:H films was $f_c = 10.0 \pm 0.5\%$. It was estimated by using the calculated integral intensities of TO phonon modes with the maxima near the frequencies ω_A, ω_I, and ω_C, respectively. The estimation procedure included the empirical calculation for the ratio of the integral cross sections of the Raman scattering in the crystalline and amorphous phases of silicon [8], and the average diameter of the silicon nanocrystals, that was taken according to the results of the analysis of the TEM photomicrographs.

The results of studying paramagnetic centers in pc-Si:H samples are given in Fig. 1, where an intense anisotropic signal can be seen in the EPR spectrum of the pc-Si:H film.

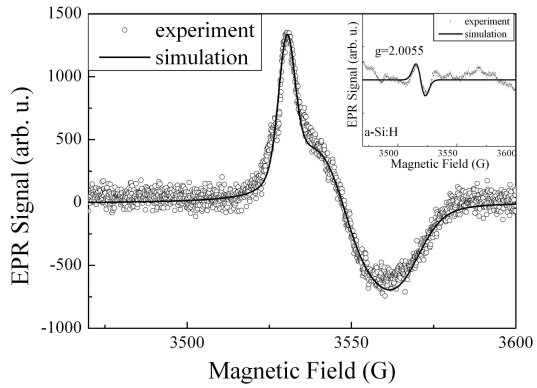

Fig 1. (Circles) EPR spectrum and (solid line) its approximation for the pc-Si:H sample. The inset shows the EPR spectrum of the a-Si:H film.

The numerical simulation of the experimental EPR spectrum has given the following g tensor and the line width values $g_1 = 1.9980$, $\Delta H_1 = 4$ G; $g_2 = 1.9885$, $\Delta H_2 = 13$ G; $g_3 = 1.9790$, $\Delta H_3 = 13$ G. To make the conclusion about the nature of the paramagnetic centers responsible for the EPR signal observed in the studied pc-Si:H films, there were performed comparative EPR studies for the hydrogenated silicon films prepared by plasma-enhanced chemical vapor deposition of monosilane under the technological conditions of the a-Si:H formation (inset in Fig. 1). The EPR signal obtained for a-Si:H was isotropic and had the following main parameters: $g = 2.0055$, $\Delta H_1 = 8$ G. This makes it possible to attribute it to the silicon dangling bonds [9]. Thus the source of the EPR signal that was observed in the pc-Si:H films is the silicon crystalline phase, namely, the electrons trapped in the states in the conduction band tail of the system of silicon nanocrystals. It is not possible to completely exclude the presence of dangling bonds in the studied structures, but it can be stated their negligibly small amount in comparison with the concentration of electrons trapped in the states of the conduction band tail.

IV. CONCLUSION

The present work shows that the nondestructive methods of Raman and EPR spectroscopy may be effectively used for the diagnostics of the structure of pc-Si:H samples. Moreover, the dramatic change in the EPR spectra under the introduction of a small fraction of silicon nanocrystals into the amorphous matrix makes EPR spectroscopy a unique tool for the express analysis of the presence of nanocrystals in the nanomodified samples of amorphous silicon.

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