

Photoluminescence of Hydrogenated Nanocrystalline Silicon Films

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Abstract — We have studied structural, electrical and photoluminescence properties of hydrogenated nanocrystalline silicon films with different crystalline volume fractions (from 0 – pristine amorphous silicon – to 55 %). The photoluminescence spectra of the films exhibit distinct features related to recombination in amorphous silicon (peak energy of about 1.35 eV) and in silicon nanocrystals (peak near 1.52 eV). When the crystalline volume fraction reached 55%, photoluminescence disappeared. Photoluminescence spectroscopy was proposed as a nondestructive method for determining of a small volume fraction of Si nanocrystals embedded in amorphous silicon.

Index Terms — Si nanocrystals, amorphous hydrogenated silicon, photoluminescence, percolation

I. INTRODUCTION

Hydrogenated nanocrystalline silicon (nc-Si:H), which consists of amorphous matrix with embedded silicon nanocrystals (nc-Si), is widely used in electronics and optoelectronics, in particular, in the production of photovoltaic cells [1] and thin film transistors [2]. nc-Si:H films with a small (10 - 15 %) volume fraction of Si nanocrystals are of particular interest. Prospects of this material are determined by the high photosensitivity typical for amorphous hydrogenated silicon (a-Si:H) and lower photo-induced degradation of electrical parameters compared to a-Si:H films [3, 4]. Photoluminescence (PL) properties of hydrogenated silicon films with silicon nanocrystals are considerably less studied than their structural, electrical and photoelectric characteristics. Among available literature data two PL peaks appear for nc-Si:H. The first peak, located near 1.3 eV, is related to tail-states transitions in a-Si:H. The second one, located near 0.9 eV, is attributed to recombination between carriers trapped at defect states at the nanocrystalline grain boundary. However, significant deviations were reported for these peaks. Thus, the focus of present work is the investigation of PL properties of a-Si:H films with different volume fractions of the nanocrystalline inclusions.

II. EXPERIMENTAL

The investigated nc-Si:H films were fabricated upon the decomposition of a mixture of monosilane (SiH₄) and hydrogen (H₂) on a quartz substrate by using the very high frequency (60 MHz) plasma enhanced chemical vapor deposition reactor. The thickness of the films was 1 μm, and the temperature of substrate during the deposition – 220°C. As the hydrogen flow was increased, the films underwent an amorphous to nanocrystalline transition. The volume ratio of gases in the reactor chamber $R_H = [H_2]/[SiH_4]$ was varied as follows: $R_H = 0$ (sample R0 – reference a-Si:H film), $R_H = 5$ (sample R5), $R_H = 8$ (sample R8), $R_H = 11$ (sample R11), $R_H = 16$ (sample R16). The

structure of the films was studied by the analysis of the Raman scattering spectra measured by the micro-Raman spectrometer Horiba Jobin Ivon HR800 under the excitation of 488 nm line of Ar-ion laser. Aluminum coplanar electrodes were deposited on the surface of the films with the 0.5 mm gap. Conductivity measurements were carried out in a vacuum with residual air pressure of 10⁻³ Pa after annealing of the films at a temperature of 180°C for 15 minutes. The PL spectra were recorded using a MS-3504i (SOLAR TII) spectrograph and a CCD camera (Hamamatsu) under excitation of 364 nm line of a continuous Ar-ion laser. During the PL experiments the samples were placed into the vacuum cell of a DE-204N closed-cycle helium cryostat (Advanced Research Systems) and cooled down to the temperature of 17 K.

III. RESULTS AND DISCUSSION

The volume fraction of the crystalline phase f_c in mixed phase hydrogenated Si films was determined by the analysis of Raman spectra, which are shown in Fig. 1. As one can see, for samples R0, R5 and R8 a broad peak is observed near 480 cm⁻¹, which corresponds to the transverse optical (TO) phonon mode in the a-Si:H structure [5]. On the contrary, in the spectra for samples R11 and R16 one can observe a sharp maximum near 520.5 cm⁻¹ which corresponds to the TO phonons in the crystalline silicon [6]. For the better numerical fit of the experimental spectra additional maxima have to be taken into account, namely, the maxima near the frequencies $\omega_{LA} = 310$ cm⁻¹ and $\omega_{LO} = 410$ cm⁻¹, which are attributed to the longitudinal acoustic and longitudinal optical phonon modes, respectively, in a-Si:H [7], as well as the maximum near the frequency $\omega_1 = 500$ cm⁻¹ which is related to the transverse optical phonons at the grain boundaries [8].

Contribution from amorphous phase of silicon and grain boundaries to Raman spectra of the studied films can be described by a Gaussian shape line [7]. Maximum near 520.5 cm⁻¹ was fitted according to the model of strong

spatial confinement of TO phonons, which takes place in silicon nanocrystals. Corresponding line shape and nc-Si average diameter were determined according to the equations presented in [9, 10]. The volume fraction of crystalline phase in the investigated films was determined by using the following expression [11]:

$$f = \frac{\bar{I}_C + \bar{I}_I}{c \bar{I}_A \sigma_0 + (\bar{I}_C + \bar{I}_I)}$$

where \bar{I}_C , \bar{I}_I and \bar{I}_A - integral intensities of contributions from crystalline, grain boundary and amorphous phases, respectively; $\sigma_0 = 0.1 + \exp(-d/25)$ - an empirical relationship between integral cross-sections of Raman scattering in crystalline and amorphous phases of silicon, where d - size of the nanocrystals in nanometers.

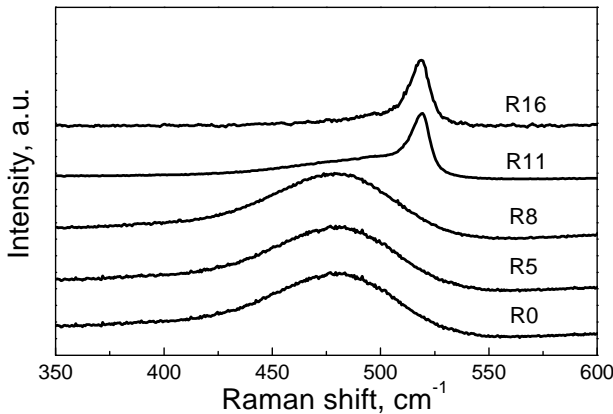


Figure 1. Raman spectra of investigated films.

Besides the crystalline volume fraction, the Raman spectra could also be used to estimate the size of Si nanocrystals. According to the red shift of the maximum of the corresponding TO phonon mode in crystalline silicon, the average nc-Si diameter can be found using the following equation [10]:

$$d = a \times \left(\frac{\Delta\omega}{A} \right)^\gamma,$$

where $\Delta\omega$ - shift of the maximum with respect to the frequency of 520.5 cm^{-1} , a - lattice constant of Si. Parameters A and γ describe the vibrational confinement due to the finite size of a nanocrystal. These parameters depend on the nc-Si shape. As the actual shape of our nanocrystals is unknown because of missing high resolution transmission electron microscopy investigations, we used in our estimations the parameters $A = 47.41 \text{ cm}^{-1}$ and $\gamma = 1.44$, obtained in [12] for Si spheres.

The results of Raman experimental data processing are presented in Fig. 2. As one can see the volume fraction of crystalline phase in studied films continuously increases with the increase of R_H , reaching the value of 55 % for the sample R16. At the same time the average size of the nanocrystals does not change significantly. It should be noted that due to the absence of an explicit form of the maximum near 520.5 cm^{-1} in the Raman spectra for the

samples R5 and R8 (Fig. 1), we could estimate the average nc-Si diameter in these samples only through our fitting procedure (in Fig. 2 these values are pointed as open squares).

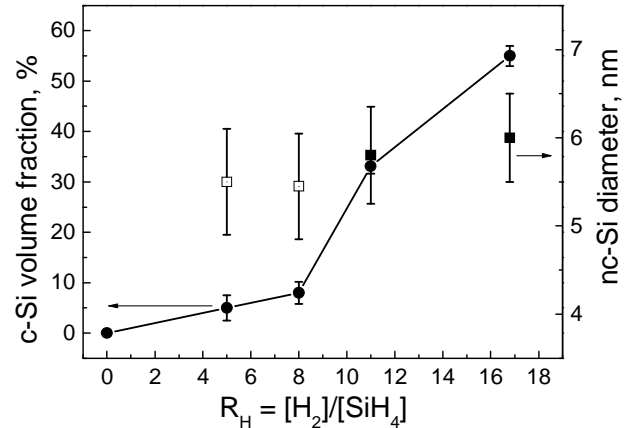


Fig. 2. The dependence of the volume fraction of the crystalline phase (circles) and the size of the nanocrystals (squares) on R_H . Line is guide for eye.

In Fig. 3 PL spectra of the investigated samples measured at 17 K are presented. Dashed lines of Gaussian shape represent the fit of the photoluminescence spectra with two maxima near 1.35 eV and 1.52 eV. As could be seen from the Fig. 3, a broad luminescence spectrum with the peak energy of about 1.35 eV and full width at the half maximum of about 0.3 eV is observed for the sample R0 (a-Si:H film) at 17 K. This spectrum is commonly attributed to the recombination between electrons trapped in localized tail states of a conduction band and holes trapped in localized tail states of a valance band [13]. These localized electronic states exist at the edges of the bands as a result of the disorder in a-Si:H. However, a small blue shift of the maximum is observed for the samples R8 and R11, which probably indicates that the order in the location of atoms in the material is improved. This could be due to the increase of the crystalline volume fraction in the samples R8 and R11. At the same time, the samples R5, R8, R11 show an additional PL maximum near the photon energy of 1.52 eV (Fig. 3). The crystalline volume fraction increase causes the increase of the integrated PL intensity near 1.52 eV. This could justify that the maximum near 1.52 eV is most likely originated from the Si nanocrystals.

It should be noted, that when the volume fraction of Si nanocrystals reaches 55% the PL disappears (sample R16), which might happen due to the initiation of nonradiative recombination channels as a result of the occurrence of the percolation way. Our experiments showed that when the crystalline volume fraction exceeds 33% (threshold value for percolation in effective medium approximation [14]) the conductivity of the material increases dramatically (more than 4 orders of magnitude). This fact demonstrates the presence of a percolation way built from silicon nanocrystals in the sample R16.

In this way, PL at low temperatures may be used as a nondestructive method for determination of a small volume fraction of Si nanocrystals in nc-Si:H films.

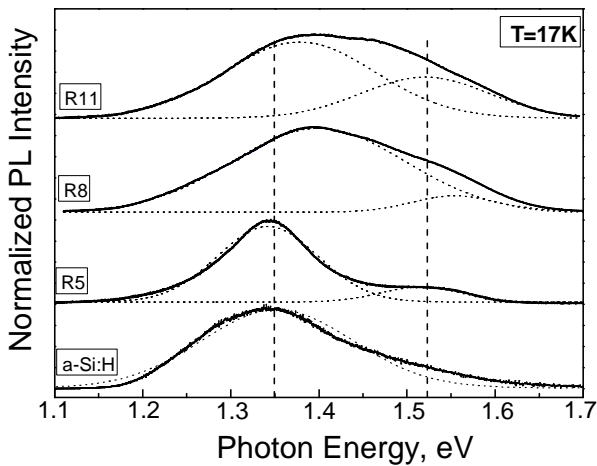


Fig. 3. Photoluminescence spectra of investigated samples at $T = 17$ K. Continuous lines represent experimental data. Dashed lines are the approximations of the peaks near 1.35 eV and 1.52 eV.

IV. CONCLUSION

The investigations of Raman scattering, as well as photoluminescence and electrical properties were performed on 1 μm thick nc-Si:H films with different crystalline volume fractions. Studied films showed two PL maxima with the peak energy of about 1.35 eV and 1.52 eV. The first maximum is related to the recombination of charge carriers localized in tail-states of a-Si:H. The integrated intensity of the peak at 1.52 eV is found to increase with the crystalline volume fraction. This peak is associated with silicon nanocrystals embedded into the matrix of amorphous silicon. When the crystalline volume fraction reaches 55% the PL disappears. Electrical measurements proved that the PL vanishing was due to the appearance of the percolation way comprised of Si nanocrystals. It was shown, that PL may be used as a nondestructive method for determination of a small volume fraction of Si nanocrystals embedded in a-Si:H.

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