

AMORPHOUS, VITREOUS, POROUS, ORGANIC, AND MICROCRYSTALLINE SEMICONDUCTORS; SEMICONDUCTOR COMPOSITES

Photoconductivity of Two-Phase Hydrogenated Silicon Films

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Abstract—Electrical, photoelectric, and optical properties of hydrogenated amorphous silicon films with various ratios between the nanocrystalline and amorphous phases in the structure of the material have been studied. On passing from an amorphous to a nanocrystalline structure, the room-temperature conductivity of the films increases by more than five orders of magnitude. With increasing fraction of the nanocrystalline component in the film structure, the steady-state photoconductivity varies nonmonotonically and is determined by the variation in the carrier mobility and lifetime. Introduction of a small fraction of nanocrystals into the amorphous matrix leads to a decrease in the absorption in the defect-related part of the spectrum and, accordingly, to a lower concentration of dangling bonds, which are the main recombination centers in amorphous hydrogenated silicon. At the same time, the photoconductivity in these films becomes lower, which may be due to appearance of new centers that are related to nanocrystals and reduce the lifetime of nonequilibrium carriers.

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1. INTRODUCTION

Hydrogenated films of amorphous (*a*-Si:H) and nanocrystalline (*nc*-Si:H) silicon are widely used to develop electronic and optoelectronic devices and, in particular, field-effect transistors and solar cells. In recent years, steadily increasing interest has been attracted to hydrogenated silicon films with two-phase structure composed of silicon nanocrystals in an amorphous silicon matrix. These materials combine high photosensitivity, which is characteristic of amorphous hydrogenated silicon, and better, compared with *a*-Si:H, stability of parameters under exposure to light [1–3]. This makes it possible to regard two-phase films of hydrogenated silicon as a promising material for optoelectronics. The physical properties of films of this kind heavily depend on the ratio between the nanocrystalline and amorphous phases in their structure. The photoelectric properties of hydrogenated silicon films with a two-phase structure [4] have been studied to a considerably lesser extent, compared with their electrical and optical properties (see, e.g., [5]). Therefore, we report in this communication on a study of the photoelectric properties of hydrogenated silicon films with a varied fraction of the nanocrystalline phase in the amorphous host and their correlation with the electrical and optical properties.

2. SAMPLES STUDIED AND MEASUREMENT PROCEDURE

Films with a thickness of 1 μm were produced at the Institute of Semiconductors, Chinese Academy of Sciences (Beijing), by decomposition of a mixture of monosilane (SiH₄) and hydrogen (H₂) in a high-frequency glow discharge plasma at a substrate (quartz) temperature of 220°C. The volume ratio of the gases in the reaction chamber, $R_H = [H_2]/[SiH_4]$, was varied from 5 to 40. The designations of the samples obtained and the corresponding values of R_H are listed in the table. The structural information about the films was obtained by analysis of their Raman spectra measured with a Horiba Jobin Yvon HR800 micro-Raman spectrometer under excitation with light at a wavelength of 488 nm. The conductivity, photoconductivity, and spectral dependences of the absorption coefficient were measured in vacuum at a residual pressure of 10⁻³ Pa on annealing the films at a temperature of

Volume ratio R_H between hydrogen and monosilane, used to obtain the samples under study, and the fraction X_C of the nanocrystalline phase in the structure of the films

Sample	R5	R8	R11	R15	R16	R40
$R_H = [H_2]/[SiH_4]$	5	8	11	15.2	16.8	40
$X_C, \%$	<10	<10	20	45	55	80

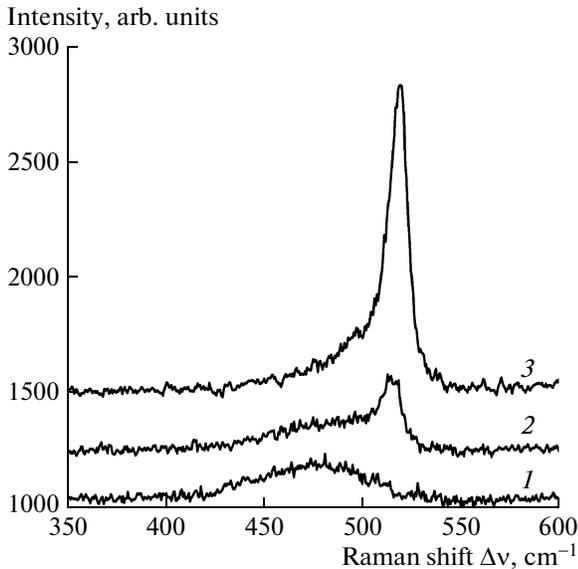


Fig. 1. Raman spectra of films obtained at $R_H = (1)$ 5, (2) 16.8, and (3) 40.

180°C for 15 min. For electrical and photoelectric measurements, aluminum contacts spaced by 0.5 mm were deposited onto the film surface.

3. MEASUREMENT RESULTS AND DISCUSSION

The Raman spectra of some of the samples are shown in Fig. 1. The Raman spectra of the two-phase films are formed by three Gaussian lines corresponding to silicon nanocrystals (Raman shift $\Delta\nu = 510\text{--}520\text{ cm}^{-1}$, I_C), amorphous phase ($\Delta\nu = 480\text{ cm}^{-1}$, I_A), and nanocrystal (grain) boundaries ($\Delta\nu = 500\text{ cm}^{-1}$, I_{GB}) [6]. The volume fraction X_C of the nanocrystalline phase is evaluated by approximating the spectra with a superposition of the three above Raman modes and subsequently calculating the ratio between the corresponding sums of their integrated intensities, $X_C = (I_C + I_{GB}) / (I_C + I_{GB} + I_A)$ [6]. The values of X_C obtained for the films under study are listed in the table. It can be seen that the fraction of the nanocrystalline phase in the films increases with R_H . The small volume of nanocrystals in the structure of samples R5 and R8 gave no way to determine X_C for these films. Nevertheless, it can be supposed that the concentration of nanocrystals in film R8 exceeds that in film R5. It is noteworthy here that, according to [6], the size of nanocrystals in films of this kind is 3–4 nm.

Figure 2 shows the temperature dependences of the conductivity (σ_d) and steady-state photoconductivity ($\Delta\sigma_{ph}$) of the films under study. It can be seen that, in the temperature range $T = 300\text{--}450\text{ K}$, the temperature dependences of σ_d of the films are of the Arrhenius type: $\sigma_d = \sigma_0 \exp(-E_a/k_B T)$, where σ_0 , E_a , and k_B

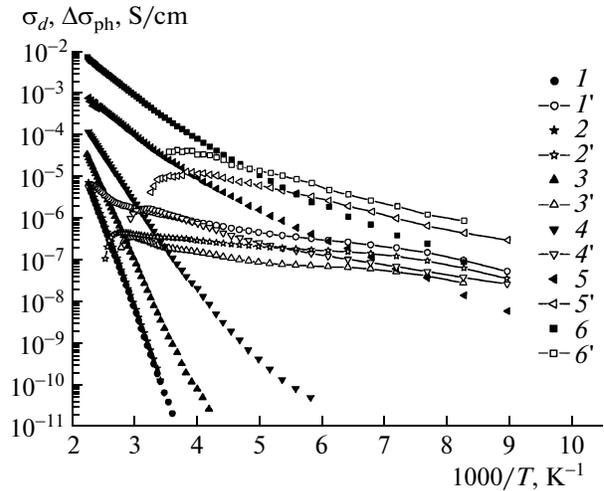


Fig. 2. Temperature dependences of ($1\text{--}6$) conductivity σ_d and ($1'\text{--}6'$) photoconductivity $\Delta\sigma_{ph}$ of the films under study. Samples: ($1, 1'$) R5, ($2, 2'$) R8, ($3, 3'$) R11, ($4, 4'$) R15, ($5, 5'$) R16, and ($6, 6'$) R40.

are the preexponential factor, activation energy, and Boltzmann constant, respectively. As R_H , and accordingly X_C , increase, the conductivity of the films grows and the activation energy E_a decreases. The steady-state photoconductivity of all the films, measured at a photon energy $h\nu = 1.85\text{ eV}$ and incident light intensity of $10^{14}\text{ cm}^{-2}\text{ s}^{-1}$, steadily grows with temperature in the range $T = 110\text{--}280\text{ K}$.

The spectral dependences of the absorption coefficient (α_{cpm}) were measured by the constant-photocurrent method [7] under steady illumination. Figure 3 shows the $\alpha_{cpm}(h\nu)$ dependences normalized to the

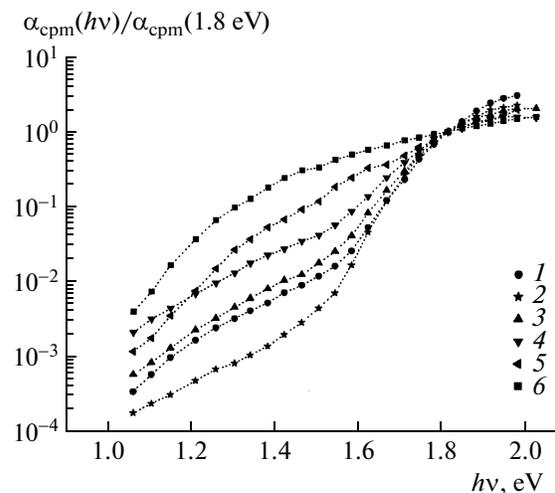


Fig. 3. Spectral dependences of the absorption coefficient in relative units, $\alpha_{cpm}(h\nu)/\alpha_{cpm}(1.8\text{ eV})$, obtained using the constant-photocurrent method. Samples: (1) R5, (2) R8, (3) R11, (4) R15, (5) R16, and (6) R40.

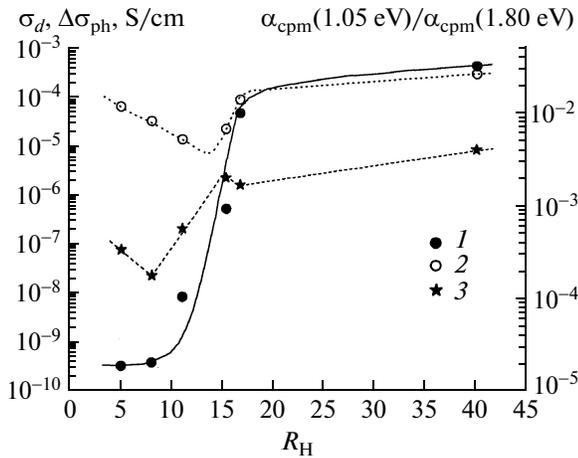


Fig. 4. Dependences of (1) conductivity σ_d and (2) photoconductivity $\Delta\sigma_{ph}$ at room temperature and (3) relative absorption coefficient on R_H at $h\nu = 1.05$ eV, $\alpha_{cpm}(1.05 \text{ eV})/\alpha_{cpm}(1.80 \text{ eV})$.

absorption coefficient at $h\nu = 1.8$ eV. It is noteworthy that, according to [5], the absolute values of the absorption coefficient (α) at $h\nu = 1.8$ eV for amorphous and nanocrystalline hydrogenated silicon are close to each other. As can be seen in Fig. 3, the spectral dependences of α_{cpm} measured for films deposited at $R_H \leq 15$ correspond in nature to the dependences $\alpha(h\nu)$ observed for amorphous hydrogenated silicon. At the same time, for films obtained at $R_H \geq 16$, the type of the experimentally measured spectral dependences of α_{cpm} is close to that observed for nanocrystalline hydrogenated silicon [5]. Because the constant-photocurrent method records the absorption responsible for the photoconductivity of the material, the observed change in the spectral dependence of α_{cpm} with increasing R_H is due to an increase in the contribution of the nanocrystalline phase to the photoconductivity of the films under study.

Let us consider the results obtained. The dependence of the room-temperature conductivity of the films on R_H is shown in Fig. 4. The maximum increase in the conductivity is observed as R_H is raised from 11 to 16, which corresponds, according to the data for X_C in the table, to the range in which the structure of the films changes from amorphous to nanocrystalline. Figure 4 also shows values of the photoconductivity of the films under study measured at room temperature with the films illuminated with an incandescent lamp (40 mW cm^{-2}) through a thermal filter. It can be seen that, in contrast to the dependence $\sigma_d(R_H)$, the dependence of $\Delta\sigma_{ph}$ on R_H and, accordingly, on the fraction of the nanocrystalline phase in the film is nonmonotonic. It is noteworthy that, for films with a small fraction of the nanocrystalline phase, the photoconductivity decreases as R_H becomes larger.

Most studies concerned with *a*-Si:H and *nc*-Si:H use the absorption coefficient at photon energies lower

than 1.2 eV as a parameter describing how the concentration of dangling bonds varies in the materials under consideration [8, 9]. Figure 4 shows values of $\alpha_{cpm}(1.05 \text{ eV})$ in relative units measured for the films studied. For films deposited at $R_H = 8-15$, the value of $\alpha_{cpm}(1.05 \text{ eV})/\alpha_{cpm}(1.80 \text{ eV})$ increases as R_H is raised and, accordingly, X_C becomes larger. The absorption decreases for sample R16 and then increases for sample R40. A similar nonmonotonic variation of $\alpha_{cpm}(1.0 \text{ eV})$ with increasing fraction of the nanocrystalline phase was obtained in [5]. In our opinion, a possible consequence of the transformation of nonequilibrium carrier generation and transport processes upon a change of the film structure is that the behavior of $\alpha_{cpm}(1.05 \text{ eV})$ in the range $R_H = 8-16$, in which the structure of the material is appreciably modified, may fail to reflect changes in the concentration of dangling bonds. At the same time, it is of interest to compare the spectral dependences of α_{cpm} in the defect-related spectral range ($h\nu < 1.4$ eV) for films with low concentrations of nanocrystalline inclusions, namely, for samples R5 and R8. In these films, the carrier generation and transport are governed by the amorphous host. As can be seen in Figs. 3 and 4, the absorption in sample R8 in the defect-related spectral range is lower than that of sample R5. A similar decrease in the absorption at $h\nu < 1.4$ eV in amorphous hydrogenated silicon films with a low concentration of nanocrystals introduced into the structure, compared with *a*-Si:H films, was observed in [3]. It was also noted in [4, 10] that the concentration of spins associated with dangling bonds in amorphous hydrogenated silicon decreases upon introduction of silicon nanocrystals into the structure. It was suggested that the decrease in the concentration of dangling bonds in this material, named protocrystalline silicon, is due to a weaker structural disorder in the films [1].

Let us consider how the photoconductivity varies with the structure of the films. The nonmonotonic variation of $\Delta\sigma_{ph}$ with R_H in Fig. 4 is close to the dependence of the carrier mobility in a two-phase structure on the volume fraction of the phase with a high conductivity, calculated [11] for a structure constituted by phases with high and low conductivity. At the same time, the variation in the photoconductivity with increasing fraction of the nanocrystalline phase in the films under study is presumably caused both by the change in the mobility of nonequilibrium carriers and by transformation of recombination mechanisms and change in the concentration of recombination centers. It is of interest in this regard to compare the photoconductivities for films with a low fraction of nanocrystalline inclusions, R5 and R8, in which variation in the lifetime of nonequilibrium carriers is presumably the key factor governing changes in $\Delta\sigma_{ph}$. It is known that the main recombination centers in undoped *a*-Si:H films are dangling bonds the energy states of which are responsible for the absorption in the defect-related spectral range ($h\nu < 1.4$ eV). As already

noted, the absorption in this spectral range in sample R8 is lower than that in sample R5. This indicates that the concentration of dangling bonds in sample R8 is lower than that in sample R5. At the same time, the photoconductivity of sample R5 exceeds that of sample R8. It can be suggested that the value of $\Delta\sigma_{ph}$ for R8 is smaller because introduction of nanocrystals into the amorphous host gives rise to new centers, which change recombination processes and reduce the lifetime of nonequilibrium carriers. In this case, the energy states of these centers must be located in the upper half of the mobility gap above the Fermi level to give no contribution to the absorption measured by the constant-photocurrent method.

4. CONCLUSIONS

Thus, this study showed that an increase in the fraction of the nanocrystalline phase in two-phase hydrogenated silicon films leads to a nonmonotonic variation in the photoconductivity of the material. This variation is determined by changes in the mobility and recombination mechanisms of nonequilibrium carriers upon transformations of the film structure. Introduction of a small fraction of nanocrystals into the amorphous host (protocrystalline silicon) reduces the absorption in the defect-related spectral range, which points to a decrease in the concentration of dangling bonds, the main recombination centers in films of amorphous hydrogenated silicon. At the same time, a decrease in the photoconductivity is observed in these films, which may be due to the appearance of new centers associated with nanocrystals and reduction of the lifetime of nonequilibrium carriers.

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REFERENCES

1. S. Guha, J. Yang, D. L. Williamson, Y. Lubianiker, J. D. Cohen, and A. H. Mahan, *Appl. Phys. Lett.* **74**, 1860 (1999).
2. J. Y. Ahn, K. H. Jun, K. S. Lim, and M. Konagai, *Appl. Phys. Lett.* **82**, 1718 (2003).
3. C. R. Wronski, J. M. Pearce, J. Deng, V. Vlahos, and R. W. Collins, *Thin Sol. Films* **451–452**, 470 (2004).
4. T. Kamei, P. Stradins, and A. Matsuda, *Appl. Phys. Lett.* **74**, 1707 (1999).
5. J. Kocka, T. Mates, M. Ledinsky, H. Stuchlikova, J. Stuchlik, and A. Fejfar, *J. Non-Cryst. Sol.* **352**, 1097 (2006).
6. X. Hao, X. Liao, X. Zeng, H. Diao, and G. Kong, *J. Non-Cryst. Sol.* **352**, 1904 (2006).
7. C. Main, S. Reynolds, I. Zrinscak, and A. Merazga, *J. Non-Cryst. Sol.* **338–340**, 228 (2004).
8. N. Wirsch, F. Finger, T. J. McMahon, and M. Vanecek, *J. Non-Cryst. Sol.* **137–138**, 347 (1991).
9. S. Klein, F. Finger, R. Carius, T. Dylla, and J. Klomfass, *J. Appl. Phys.* **102**, 103501 (2007).
10. O. Astakhov, R. Carius, F. Finger, Y. Petrusenko, V. Borysenko, and D. Barankov, *Phys. Rev. B* **79**, 104205 (2009).
11. H. Overhof and M. Otte, in *Future Directions in Thin Film Science and Technology*, Ed. by J. M. Marshall, N. Kirov, and A. Vavrek, and J. M. Maud (World Sci., Singapore, 1996), p. 23.

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