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# Photoluminescent films of nanocrystalline silicon doped with metals

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**Abstract.** Effects of electropositive (Au, Ag, Cu) and electronegative (Al, In) metal impurities are investigated from the viewpoint of photoluminescent and electronic properties of nanocrystalline silicon films prepared by laser ablation when depositing them onto a silicon substrate. Measured are time-resolved photoluminescence spectra and temperature dependences of the capacitance photovoltage. It was ascertained that only Au could essentially increase intensity and stability of photoluminescence, increase its relaxation time by three orders of magnitude as well as decrease the density of states near the film-substrate boundary. It has been shown that the metal impurities provide an essential effect on photovoltage arising in films of nanocrystalline Si as well as the capture of non-equilibrium electrons by traps both in films themselves and at the substrate boundary.

**Keywords:** nanocrystalline silicon films, photoluminescence, capacitance photovoltage, metal doping, boundary electron states, electron traps.

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## 1. Introduction

Photoluminescence (PL) in nanocrystalline silicon (nc-Si) in the visible spectral range at the room temperature is a subject of intensive investigations connected with the development of conceptions about processes in quantum-confined nanostructures and potential opportunity of applying them in silicon optoelectronics. In respective works, the main attention is focused on ascertaining the nature of visible PL in structures containing silicon nanocrystals (NC), namely in porous silicon (por-Si) prepared by chemical or electrochemical etching a silicon (c-Si) substrate, and in nc-Si films formed by different ways (chemical deposition in a glow discharge, silicon implantation into dielectrics, cathode sputtering, laser ablation, etc.).

There are a few works where studied is the influence of doping with various impurities on properties of these structures, especially on their PL. However, the results of available works (see, for instance [1-15]) are indicative of a considerable role inherent to impurity atoms at the surface and in the bulk of SiNC as well as in a matrix containing them. More specifically, an essential influence of hydrogen and oxygen on PL properties of por-Si is found in [1-4]. Effective and stable PL was observed when introducing chlorine [5,6] and manganese [7] into

por-Si, as well as treating it in acetone vapours, which resulted in carbonization of nc-Si [8]. Authors of [9] reported about PL bands caused by introduction of samarium into the  $\text{SiO}_x$  matrix of por-Si.

There are data concerning the influence of impurities on nc-Si film properties. For example, in [10] found was that implantation of nitrogen, in addition to silicon, increases the NC amount, rises PL intensity and shifts PL peak into the short-wave side of the spectrum. When doping SiNC with gallium and boron they observed PL vanishing [11, 12]. A growth of PL intensity with increasing concentration of phosphorus passivating the defects at the boundary of nanocrystall-borosilicate glass matrix was observed in [13], and that connected with phosphorus introduction into nc-Si films prepared by implantation of Si into  $\text{SiO}_2$  was shown in [14]. Authors [15] found that oxidation of porous nc-Si films prepared by laser ablation resulted in growth of visible PL intensity, shift of its spectrum into the red side and considerable increase of its relaxation time. They made the conclusion that oxygen not only depresses the non-radiative recombination channel, but promotes the increase of excitonic PL share due to the effect of dielectric amplification.

In this work, we studied the influence of impurities comprising electropositive (Au, Ag, Cu) and electronegative (In, Al) metals (i.e. possessing respectively positive or negative standard potentials relatively to silicon [16])

on PL and electronic properties of nc-Si films obtained by laser ablation and deposited on p-Si substrate. Spectral PL dependences were measured as the time-resolved ones. Temperature dependences of the capacitance photovoltage caused by illumination of the nc-Si/p-Si system with pulses of white and red light. These photovoltage measurements enables to determine temperature dependences of a p-Si substrate boundary potential, density of boundary electronic states (BES) there, temperature dependences of a capacitance photovoltage in nc-Si films as well as analogous dependences for concentrations of non-equilibrium carriers captured by traps both in the nc-Si film and at the boundary nc-Si/p-Si.

Such investigations are important for ascertaining electronic processes taking place in this nc-Si/p-Si structure as well as for intentional formation of nc-Si/p-Si structures with definite electronic and photoelectronic properties.

## 2. Methods of preparation of nc-Si films doped with metals

Reasons for choosing metals. Photoluminescent nc-Si films were prepared using the laser ablation method [15]. The beam of YAG:Nd<sup>3+</sup> laser (operating in the Q-switched mode with the wavelength  $\lambda=1.06\ \mu\text{m}$ , pulse energy density  $20\ \text{J}/\text{cm}^2$ , pulse duration 10 ns, pulse frequency 25 Hz) scanned the target of p-Si labelled as KDB-10. To dope films with metals, the c-Si target was covered by a thin film consisting of one from the row: Au, Ag, Cu, Al, In. The target and p-Si substrate positioned in the plane of this target were placed into a vacuum chamber filled by Ar with a pressure close to 13 Pa. Interaction of Ar atoms with particles of the erosion plume resulted in deposition of the n-Si film from the reverse flow of plume particles. The rate of film deposition was approximately 15-20 nm/min, their thickness 500 nm, and porosity 40%. Before insertion of p-Si substrate into the vacuum chamber, it was processed in HF solution and then washed by distilled water for a short time. As a consequence, it had mainly a hydride cover [17].

The erosion plume contains atoms, ions and clusters of silicon as well as atoms and ions of metal. The atoms and ions of metal, like to silicon particles, can be deposited onto p-Si substrate and interact with NC Si both in the plume and on the substrate, which may result in passivation of broken silicon bonds on NC surface. Therefore, to ascertain the character of metal influence on nc-Si film properties, we chose metals with the positive (Au, Cu, Ag) and negative (Al, In) standard potentials rela-

tively to silicon [16]. The Table contains data of the first ionization potentials and electron affinity energies both for these metals and silicon as well as oxygen. It is seen from the Table that Au atoms and ions should effectively take electrons away from Si atoms. In doing so, first of all, they should capture electrons from Si atoms having broken bonds, the latter being passivated through creation of Si-Me bonds [16]. Experimental evidences of effective passivation of broken bonds by Au ions were obtained by one of the authors [18] when investigating electron spin resonance in c-Si powders. Passivation of the broken bonds in Si NC can be also reached using Ag and Cu ions, although the ionization energy of their atoms is slightly less than that of Si atom. It is connected with the fact that adsorption of Ag and Cu atoms takes place at those Si NC, for which the energy of tearing electron off is less than ionization energy of Si atoms and approaches in its value to the work function inherent to single-crystalline silicon. Passivation of broken bonds by Au, Ag, Cu ions is capable to increase PL intensity of nc-Si films due to depression of fast surface component in non-radiative recombination.

Further adsorption of electropositive metal ions on Si NC surface is accompanied by capture of valent electrons from Si, which is equivalent to a break of Si-Si bonds [16]. The latter promotes binding residual oxygen in the vacuum chamber with surface silicon atoms. Catalytic activation of the oxidizing process by metal results in preferential creation of SiO<sub>2</sub> layer on Si NC surface instead of SiO<sub>x</sub> (0<x<2) layer. It must yield also in increasing PL intensity as a consequence of: i) an increasing height of a potential barrier; ii) a growing role of excitonic PL due to the effect of dielectric amplification (as the dielectric permittivity of SiO<sub>2</sub> is lower than that of SiO<sub>x</sub>); iii) Si NC with sizes more than 5 nm could be included into the radiation process as it caused by reduction of their sizes when being oxidized, etc.

Ions of electronegative metals Al and In should not passivate broken bonds, but doping nc-Si films with these metals could change their electronic properties.

Previous experiments with the most effective impurity Au enabled to ascertain that the optimum thickness of the metal film on a p-Si target should be some 80 nm. PL intensity and its relaxation time in the nc-Si/p-Si structure were increased the most effectively at this thickness. The less film thickness have insufficient Au amounts to passivate most of broken bonds, the larger ones promote leakage of non-equilibrium charge carriers from Si NCs through Au clusters. Therefore, as a rule, we used metal film thickness of several tens of nanometers.

**Table. Ionization energies and electron affinity of oxygen, silicon and metal atoms**

Element	O	Si	Au	Ag	Cu	Al	In
First ionization energy, eV	13.62	8.15	9.26	7.58	7.72	5.98	5.78
Electron affinity of atom, eV	1.47	1.40	2.31	1.30	1.23	0.44	0.30

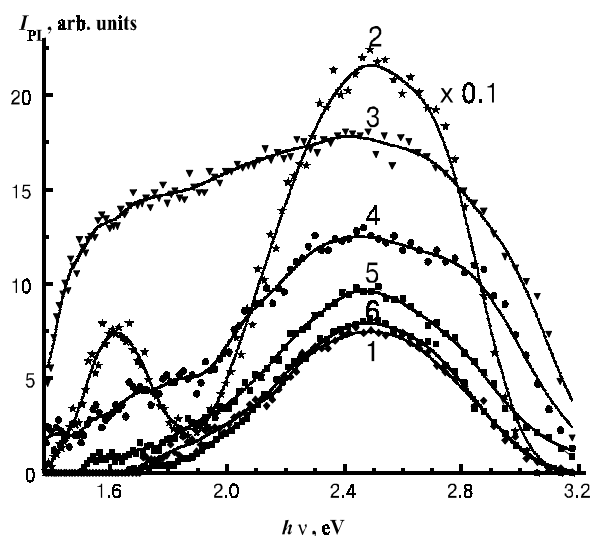


Fig. 1a. PL spectra measured at the first strobe ( $0 < t < 250$  ns) for the following films: non-doped (1) and doped with impurities of Au (2), Ag (3), Cu (4), Al (5), In (6).

### 3. Methods of measurements

The obtained nc-Si/p-Si structures were used for measurements of time-resolved PL spectra [15] and photovoltage temperature dependences. The photovoltage was excited by illumination of the structure with high intensity light pulses [19]. PL excitation was made by the emission of nitrogen laser ( $\lambda = 337$  nm,  $\tau = 8$  ns). Strobed signal registration was realized using a photon counting mode. The minimum duration of the strobe providing accumulation of photons was 250 ns. Spectra of the fast ( $\tau < 250$  ns) PL component were measured by combining strobe and laser pulse fronts. Relaxation times less than 50 ns were estimated using oscilloscope. Subsequent in time spectra were recorded using the strobe delay relatively to a laser pulse by the integer of the strobe durations. When measuring maximum relaxation times of tens of microseconds, both strobe width and its delay were increased arbitrarily. PL instability was estimated through measuring changes in PL intensity with time using laser excitation or after a long exposure of samples in ambient atmosphere.

To measure a photovoltage, our vacuum cryostat was equipped by a measuring capacitor consisting of the system p-Si/nc-Si film that was pressed to a mica layer. Another side of this film was covered by a semitransparent conducting layer  $\text{SnO}_2 < \text{Sb} >$ . We measured a photovoltage arising in the substrate when illuminating the capacitor by red light pulses (in doing so, we used the filter transmitting light within the range 700-2700 nm), this light being practically not absorbed in the nc-Si film, and a total photovoltage in the film and substrate that arises when using white light pulses. Under red light, the photovoltage  $V_{ph}$  measured at  $\text{SnO}_2 < \text{Sb} >$  electrode is equal with the reverse sign to the boundary potential of the p-Si substrate  $\phi_s$ . The photovoltage was recorded us-

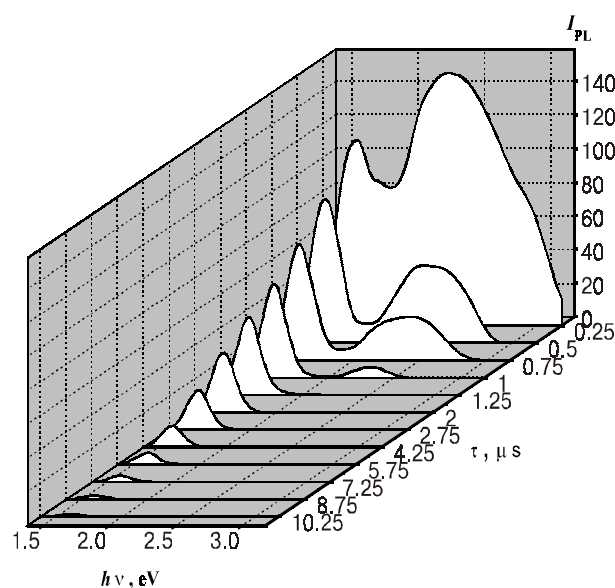


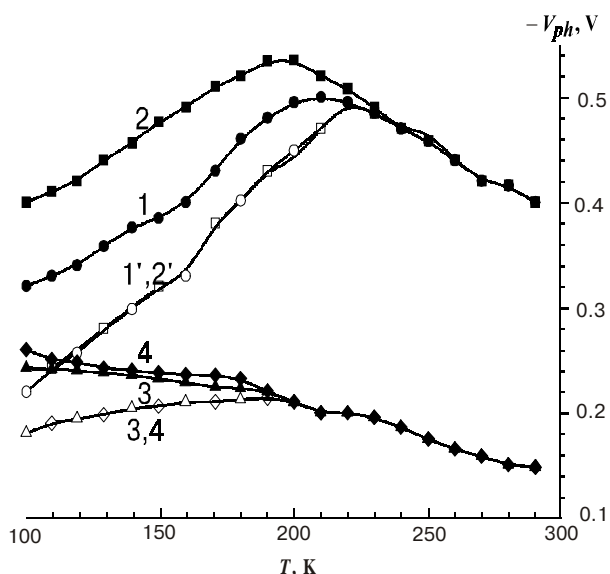
Fig. 1b. Time-resolved PL spectra for nc-Si < Au > films.

ing a memory oscilloscope. As a source of light, we used a flash lamp ISSh-100 with the pulse duration of 10  $\mu\text{s}$  and its intensity  $10^{21}$  photon/cm<sup>2</sup>s. The flash lamp could operate in the mode of single pulses or their trains with the frequency 1 Hz. In more details, this method of photovoltage measurements was described earlier [19].

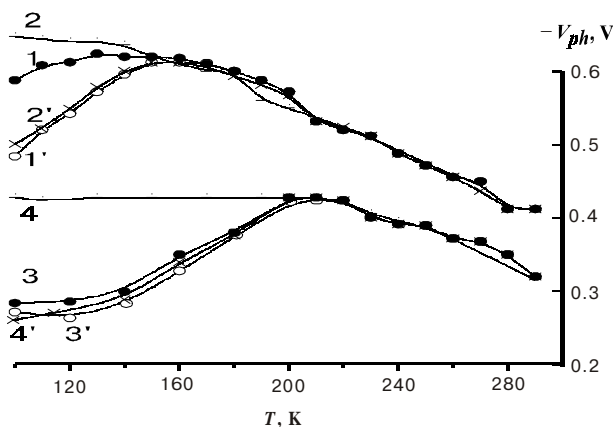
### 4. Experimental results and discussion

Shown in Fig. 1a are PL spectra measured during the first strobe ( $0 < \tau < 250$  ns) for non-doped (curve 1) and doped with Au, Ag, Cu, Al, In films (curves 2 to 6, respectively). All films, excepting that doped with Au, were characterized only by short PL relaxation times ( $\tau < 50$  ns). It is seen from Fig. 1a that PL spectra are wide and cover the wavelength range 400 to 900 nm with PL peaks close to 400-500 nm. Spectral shapes of non-doped and doped with Al and In nc-Si films are similar. When doping with Au, Ag, Cu, spectra show long-wave components (700-900 nm), they being pronounced more and more in the series Cu, Ag, Au. The same series is valid to the PL intensity: the highest intensity was observed in films doped with Au, the less one – in those doped with Ag, and the lowest – Cu. PL spectra of non-doped and doped with Al and In had more lower intensity but approximately equal to each other.

The only nc-Si films doped with Au showed PL components slower than 50 ns, their duration could reach 10-20  $\mu\text{s}$  (Fig. 1b). There are four bands with peaks near to 3.0, 2.6, 2.3 and 1.6 eV in the more fast ( $\tau < 250$  ns) component. The intensity of the most short-wave band peaking at 415 nm (3.0 eV) being higher than that of the most long-wave one at 775 nm (1.6 eV). With increasing relaxation time, the band with the peak at 3 eV vanishes (already at  $\tau > 500$  ns), while the intensity of the long-wave band becomes higher than that of the short-wave



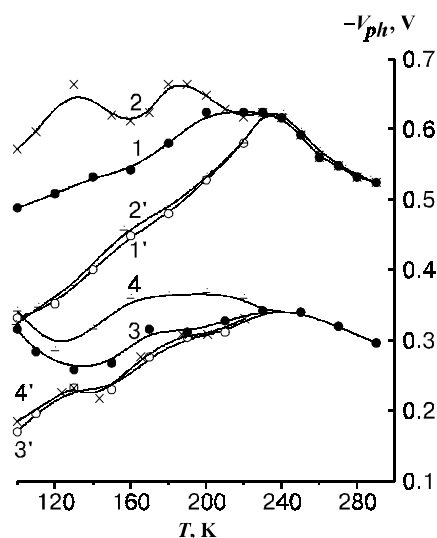
**Fig. 2.** Temperature dependences of photovoltages inherent to nc-Si/p-Si structures with non-doped (1, 1', 2, 2') and Au-doped (3, 3', 4, 4') films. 1,3 – the first pulse of red light, 1', 3' – the second one; 2, 4 – the first white light pulse, 2', 4' – the second one.



**Fig. 3.** Temperature dependences of photovoltages inherent to nc-Si/p-Si structures with Cu-doped (1, 1', 2, 2') and Ag-doped (3, 3', 4, 4') films. 1, 3 – the first red light pulse, 1', 3' – the second one; 2, 4 – the first white light pulse, 2', 4' – the second one.

one and at long times it remains alone. As a rule, a similar character of PL spectra transformations was observed in por-Si [1,2].

As a quantum efficiency value of PL for all investigated films is equal to several percents, the measured PL relaxation times are times of non-radiative recombination of non-equilibrium charge carriers. The results shown in Fig. 1b are indicative of the fact that the non-radiative recombination time in the films doped with Au is by three orders of magnitude larger than those in all other films. The other electropositive metals (Ag, Cu) increased the non-radiative recombination time too, but only by 2 to 4 times as compared with its value for the non-doped nc-Si films. Thus, the only Au can considerably depress the



**Fig. 4.** Temperature dependences of photovoltages characterizing the nc-Si/p-Si structures with In-doped (1, 1', 2, 2') and Al-doped (3, 3', 4, 4') films. 1, 3 – the first and 1', 3' – the second pulses of red light; 2, 4 and 2', 4' – the first and second white light pulses, respectively.

channel of fast non-radiative recombination, which results in increasing PL intensity. In such a case, passivation of large-dimension Si NCs is more effective than that of the smaller ones. That promotes more essential growth of the long-wave band PL intensity. This growth of the long-wave PL intensity is also caused by increasing excitonic radiation recombination. The exciton energy growth with the increasing depth of the potential well caused SiO<sub>2</sub> layer on NCs instead of the SiO<sub>x</sub> one.

In this case of non-doped films, continuously illuminated by the nitrogen laser, PL intensity was reduced by 40-45% for the first 20 minutes of irradiation, which was intrinsic to nc-Si/p-Si structures. But a prolonged (half-year) storage of these films in air resulted in 30% increase of PL intensity. The most pronounced effect of PL intensity stabilization was obtained for films doped with Au. In twenty minutes of continuous laser irradiation, PL intensity of these structures was reduced by no more than 5% in its magnitude, while being stored in air for a long time it was also increased but by no more than 5-10%. Doping nc-Si films with other metals has considerably less effect on stabilization of PL intensity.

Temperature dependences of the capacitor photovoltage  $V_{ph}$  were measured alternating illumination of nc-Si/p-Si structures with pulses of white and red light. In Figs 2-4 shown are  $V_{ph}(T)$  dependences (the photovoltage sign at the semitransparent SnO<sub>2</sub><Sb> electrode was negative) for structures non-doped and doped with Au, with electropositive metals Ag and Cu, as well as electronegative metals In and Al. The curves 1 and 3 were measured under illumination by the first pulse, curves 1' and 3' – when illuminating by the second pulses of red light, while the curves 2,4 and 2',4' are obtained, respec-

tively, under illumination by the first and second pulses of white light. The curves 1, 1', 3, 3' reflect the change of the boundary potential of the p-Si substrate  $\varphi_s = -V_{ph}$  with temperature. At definite temperatures varying, to some extent, for different structures, when these temperatures are reduced,  $V_{ph}$  values measured at second or any further light pulse within their train were less in their magnitudes. It means that at these lowered temperatures one can observe some photomemory effects [16] connected with the electron capture by the traps located at the substrate-film boundary (when illuminating by the red light) or both by these traps and traps in the nc-Si film (when using white light). When the photomemory effect was present, we performed measurements using the way of heating the samples as it was described earlier [19].

It is seen from Figs 2-4 that the  $V_{ph}$  values at  $T > 200$ -220 K corresponding to illumination with red and white light coincide to each other. This means that any sizable photovoltage does not arise in these nc-Si films at such temperatures when using white illumination. An observed growth of  $|V_{ph}|$  with lowering temperatures in this field is connected with charging the BES of the p-Si substrate by holes when shifting the Fermi level in silicon towards  $v$ -band. Having fulfilled calculations like those made in [20], we showed that the Fermi level in p-Si near the boundary with the initial non-doped with metals nc-Si film is practically stabilized at the silicon surface by the large BES concentration (it is larger than  $1 \cdot 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$  at the level of 0.1 eV higher than the middle of the forbidden gap  $E_i$  (i.e.,  $E_i + 0.1 \text{ eV}$ ). The pinning of the Fermi level in p-Si near the boundary with nc-Si films was also observed when changing temperature of structures doped with Ag, Cu, Al, In. While doping with Ag and Al, the Fermi level was stabilized near  $E_i$ , and using Cu – at 0.1 eV, In – at 0.2 eV higher than  $E_i$ .

As seen from  $V_{ph}(T)$  dependences represented in Figs 2 to 4 and obtained using red light (the curves 1 and 3),  $|V_{ph}|$  values begin to decrease at definite temperatures with their decreasing. This reduction of  $|V_{ph}| = \varphi_s$  is bound with a transformation of the BES system [21] due to reversible structural changes of the boundary nc-Si film – p-Si substrate. In the case of doping this structure with Al, the  $\varphi_s$  decrease is changed by its growth again at  $T < 130 \text{ K}$ , which can be bound with competitive processes of the BES system transformation and charging the traps by holes with changing temperature (Fig. 4, curve 3). In the case of the structure nc-Si/p-Si (Fig. 2, curve 3) this transformation of the BES system could be observed in all investigated temperature range from 300 down to 100 K.

Besides, as our estimations showed, doping the nc-Si/p-Si structure with Au can considerably decrease the BES density at the p-Si substrate. This results in the fact that the Fermi level position near the p-Si boundary cannot be stabilized but changes with lowering temperature in the range 300-100 K from 0.14 to 0.28 eV below  $E_i$ . Scanning the forbidden gap of the p-Si substrate with the Fermi level at its boundary due to changing the temperature enabled us to determine the BES density distribution

in the substrate. It turned out that due to doping the structure with Au there arises the whole system of BES density peaks corresponding to 0.18, 0.21 and 0.24 eV below  $E_i$  with concentrations of  $5 \cdot 10^{11}$ ,  $2.5 \cdot 10^{11}$  and  $1.2 \cdot 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ , respectively.

Thus, introduction of Au into the nc-Si/p-Si structure essentially decreases the substrate BES density in comparison with its values in non-doped and doped with Ag, Cu, Al, In structures. Earlier, when doping a Si surface with Au from its salt solutions in water and various etchants, they usually observed the growth of the surface state density [16]. Our work using another method of Au introduction into the Si surface showed the opposite result, namely, the decrease of the BES density. This fact can be explained by structural transformation of the Si surface [16] (that had preferably a hydride cover before deposition of the nc-Si film with Au) influenced by the reverse flow of Au atoms and ions deposited onto it from the erosion plume. It is also confirmed by an observed decrease of the BES density at the Si surface when we used laser ablation of the only Au target. As to the specific nature of the abovementioned BES density peaks, we cannot make a definite conclusion up to date. It is only reasonable to note that they are in the range inherent to two  $P_b$  centers at the Si-SiO<sub>2</sub> interface [22].

As seen in Figs 2-4, the difference between  $V_{ph}$  values measured under illumination by first red and white light pulses arises only at definite temperatures when the latter are decreased. It means that under definite low temperatures, the photovoltage  $V_{ph}^{nc-Si}$  arises in the nc-Si films as a difference between  $V_{ph}$  values obtained at the same temperature, if using white and red light. It is negative and coincides in its sign with the photovoltage in the p-Si substrate. Depicted in Fig. 5 are temperature dependences of the  $V_{ph}^{nc-Si}$  photovoltage in non-doped (curve 1) and doped with Au, Ag, Cu, Al, In nc-Si/p-Si structures (curves 2-6, respectively). It is seen that the  $|V_{ph}^{nc-Si}|$  photovoltage inherent to the non-doped structure appears at  $T = 220 \text{ K}$  and grows with its lowering, then reaches its maximum value at 140 K, which is followed by some decrease. The structures doped with electropositive metals Au, Ag, Cu show the same photovoltage in the nanocrystalline film at lower temperatures (190, 200 and 170 K, respectively), and its magnitude monotonically grows with decreasing temperature down to 100 K. At 200 K, the value  $|V_{ph}^{nc-Si}|$  of the Ag-doped structure is larger than that of the non-doped one, but Cu- and especially Au-doping essentially lowers the photovoltage magnitude in the film. In Al- and In-doped structures, the photovoltage arises in the films at higher temperatures (230 and 220 K, respectively) than in structures doped with electropositive metals. When using electronegative metals Al and In,  $|V_{ph}^{nc-Si}|$  dependences become non-monotonic and have extrema at definite temperatures (Fig. 5, curves 5 and 6).

Photovoltage appearance itself in the nc-Si films at lowered temperatures and its change with temperature enables to assume that its existence is caused by reversible structural strains in the films, which is valid at low-

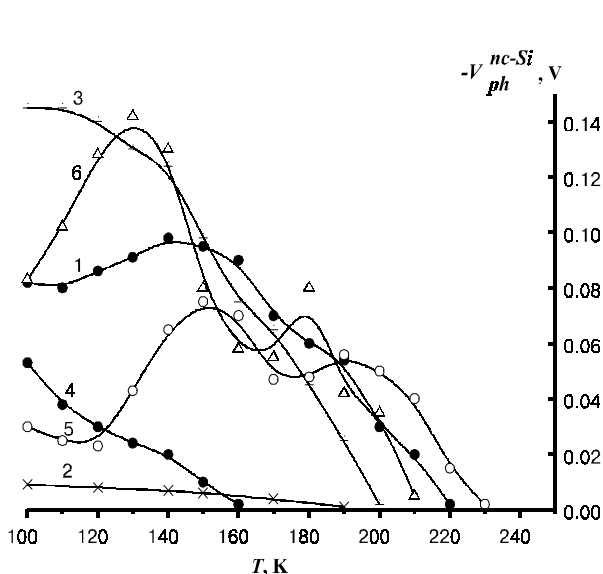


Fig. 5. Temperature dependences of photovoltages  $V_{ph}^{nc-Si}$  in films: 1 - non-doped and doped with: 2 - Au, 3 - Ag, 4 - Cu, 5 - Al, 6 - In.

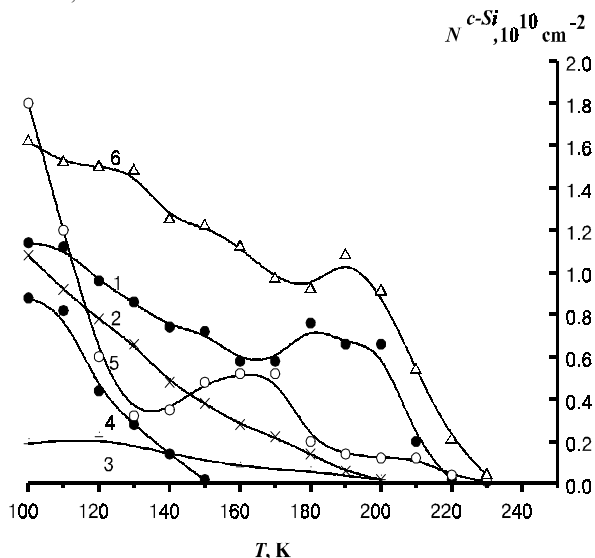


Fig. 6. Temperature dependences of amounts of electrons captured by traps in p-Si substrate when structures contain films: 1 - non-doped and doped with: 2 - Au, 3 - Ag, 4 - Cu, 5 - Al, 6 - In.

ered temperatures. These strains causes an appearance of the built-in positive charge, the value of which grows when approaching to the outer film surface. Electron-hole pairs generated by white light in these films are separated by the electric field of this charge, which causes developing the photovoltage. The lowest photovoltage in the Au-doped films testifies to the lowest strains in these films as compared with non-doped and other metal doped films. The latter agrees with the fact that the BES spectrum in the nc-Si <Au>/p-Si structure does not transform with lowering temperature, while in the non-doped and other metal doped structures the BES spectrum is considerably transformed (Figs 2-4). Non-monotonic  $V_{ph}^{nc-Si}(T)$

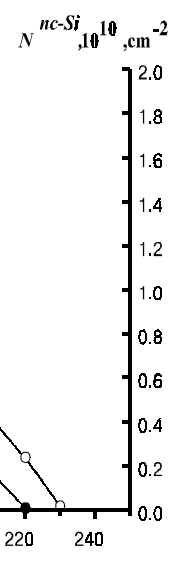


Fig. 7. Temperature dependences of amounts of electrons captured by traps in nc-Si films: 1 - non-doped and doped with: 2 - Au, 3 - Ag, 4 - Cu, 5 - Al, 6 - In.

dependences in structures doped with electronegative metals Al and In are obviously related to the presence of reversible structural transformations of various kinds in these films.

Using the difference between measured under red light curves 1 and 1', 3 and 3' (Figs 2-4), respectively, shown in Fig. 6 are calculated like [23] temperature dependences of concentrations  $N^{c-Si}$  inherent to electrons captured by boundary traps in silicon that are close to the non-doped nc-Si film (curve 1) and to Au-, Ag-, Cu-, Al-, In-doped films (curve 2 to 6, respectively). As these traps are saturated already during the first light pulse, the  $N^{c-Si}(T)$  dependences reflects also temperature dependences of concentrations for traps that capture electrons. The growth of their amount with lowering temperature is caused by more shallow traps located closer to the Si c-band, which are included into the electron capture process. Fig. 6 shows that doping the nc-Si/p-Si structure with electropositive metals lowers the trap amount of electrons in p-Si substrate, the concentration of more deep traps being mainly decreased, which are pronounced at higher temperatures. In contrast, electronegative metals Al and In increases the shallow trap concentration as compared with its value in the non-doped substrate and change to some extent the deep trap concentration, namely: Al decreases and In increases it.

Depicted in Fig. 7 are temperature dependences of concentrations  $N^{nc-Si}$  characterizing non-equilibrium electrons captured by traps located in the nc-Si films. These dependences were calculated using curves 2 and 2', 4 and 4' (Figs 2-4) measured with white light, the concentration of electrons captured by traps in the p-Si substrate being extracted. It is noteworthy that calculations of  $N^{nc-Si}$  enabled to determine the lower limit of the

captured electron amount inherent to film traps, as a potential drop created by the captured electron charge takes place not only in the substrate but in the film, too. As far as the traps in the film similar to those in the p-Si substrate are already saturated with electrons during the first white light pulse, the  $N^{\text{nc-Si}}(T)$  dependences are identical to those of concentrations characteristic to traps that capture electrons. As seen in Fig. 7, introduction of Au and Cu impurities into the films reduces essentially the trap concentrations in them, while Ag impurity increases it. The latter result constantly took place in several Ag-doped structures and distinguishes Ag influence from those of Au and Cu. In these cases, the Ag impurity always gave the lowest trap concentrations in the p-Si substrate. The  $N^{\text{nc-Si}}(T)$  dependences for Al- and In-doped structures have a non-monotonic character that, as it was mentioned above, can be explained by structural transformations of various kinds in films with changing temperatures.

Thus, as follows from measurements of photovoltage temperature dependences, the only Au impurity from all investigated metals could considerably decrease the BES density in the p-Si substrate and, at the same time, the photovoltage value in the nc-Si substrate and, at the same time, the photovoltage value in the nc-Si film as well as concentrations of traps for electrons in the p-Si substrate and nc-Si film. Besides, only Au could considerably increase the film PL intensity, its relaxation time and PL stability. To our opinion, this unique ability of Au is caused by the fact that only gold among all investigated metals possesses the larger first ionization potential atoms of its as compared to that of silicon and the larger affinity energy of its atom to the electron (see Table).

## 5. Conclusions

1. Doping the nanocrystalline Si films deposited on the p-Si substrate using laser ablation in Ar atmosphere and electropositive (Au, Ag, Cu) as well as electronegative (Al, In) metals showed that the former ones increase the PL intensity, its relaxation time and change the PL spectral characteristics due to arising the long-wave shoulder in the range 700-900 nm. Electronegative metals do not practically change the PL parameters of the nc-Si/p-Si structures.

2. The most considerable growth of PL intensity was observed after doping the structures with the Au impurity. It provides the three-order growth of the relaxation time value (from  $\tau < 50$  ns to  $\tau = 10\text{--}20$   $\mu\text{s}$ ) and an essential increase in PL stability during continuous action of laser radiation or prolonged storage of these structures in air. It is related to effective Au-passivation of centers responsible for the fast component of the surface non-radiative recombination in silicon nanocrystals, as only gold atoms have the first ionization potential and energy of electron affinity higher than silicon atoms.

3. We found an essential decrease of the boundary electron state density in the p-Si substrate when doping nc-Si/p-Si structures with gold. Other metals do

not practically change the great BES density (more than  $1 \cdot 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ ), which provides stabilization of the Fermi level position at the p-Si boundary with changing temperature.

4. With lowering temperature from 300 down to 100 K, in the range of 230-150 K there arises a photovoltage in nc-Si films that has the same sign as that in the p-Si substrate. Its value monotonically increases with further lowering temperature in structures doped with electropositive metals Au, Ag, Cu. In contrast, structures doped with electronegative metals Al and In shows non-monotonic temperature dependences (i.e., having extrema) of the photovoltage in the nc-Si film. Cu and, especially, Au impurities decrease the photovoltage in the nc-Si film, which can be related to decreasing structural strains in doped films as compared with that in the non-doped ones, when the temperature of investigated structures are lowered.

We obtained temperature dependences of concentrations inherent to electrons captured by boundary traps in the p-Si substrate and traps in the nc-Si film. Shown is that doping the nc-Si/p-Si structures with Au, Ag, Cu impurities results in decreasing density of boundary traps (especially, of the deep ones), and doping with Al and In provides the growth of the shallow trap in the p-Si substrate. Au and Cu impurities reduce the trap density in the nc-Si film.

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