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Relaxation of photovoltage in ITO-Ge-Si heterojunction with Ge nanostructured thin films

S.A. Iliash¹, Yu.V. Hyrka¹, S.V. Kondratenko¹, V.S. Lysenko², Yu.M. Kozyrev³, V.V. Lendel¹

¹Taras Shevchenko National University of Kyiv, 64/13, Volodymyrs'ka str., 01601 Kyiv, Ukraine E-mail: iliashsviatoslav@gmail.com ²Institute of Semiconductor Physics, 41, prospect Nauky, 03680 Kyiv, Ukraine

³O.O. Chuiko Institute of Surface Chemistry, 17, Generala Naumova str., 03164 Kyiv, Ukraine

Abstract. The paper focuses on experimental study of the photovoltage time decay in ITO-Ge-Si heterojunction with Ge nanostructured thin film. Kinetics under 650 nm excitation within the temperature range 80 to 290 K are successfully described by a single exponential function with temperature-dependent decay constants. Photovoltage relaxation is modeled taking into account the hopping nature of electron transport in the band of localized states.

Keywords: heterostructure, ITO-Ge-Si heterojunction, thin films, photovoltage, transient voltage.

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1. Introduction

Semiconductor nanoclusters (NCs) attract interest due to new possibilities for many electronic applications, *e.g.*, field-effect transistors, IR photodetectors, and solar cells [1-3]. The improvement in the device performance is reached by decreasing the distance between the NCs, narrowing the dispersion of NC sizes as well as changing the NCs capping material.

The nanocrystalline Ge films grown on silicon substrates are of particular interest, due to their compatibility with silicon technology. Electronic spectrum, charge carrier transport and optical properties of SiGe-based nanostructures essentially depend on the mechanical stress caused by mismatch of parameters of Si and Ge crystal lattices as well as variations in the size and composition of Ge nanostructures. This makes possibilities for creating thin films with predetermined properties for applications in optoelectronics, photovoltaics and sensors.

2. Experimental details

The molecular beam epitaxy (MBE) technique was used to prepare monolayer and multilayer Ge–Si(100) NC arrays with the clusters of various sizes and surface density. The (100) oriented plates of *p*-Si with resistivity of 7.5 Ω ·cm and diameter of 76 mm were used as substrates. The background pressure of residual gases in the MBE set-up was $6 \cdot 10^{-10}$ Torr. After desorption of the passivating Si oxide film from the Si substrate, which was exposed to a Si beam of a weak intensity and kept at 800 °C in the course of this process, a buffer Si film, about 0.1 to 0.5 µm thick, was deposited onto the Si surface. This film produces a high-contrast Si(100) 2×1 RHEED pattern typical of clean Si. The Ge nanocrystalline layers were deposited at 350 °C. The deposition rate was 0.15 nm/min for Si and 5.0 nm/min for Ge.

The ITO films $(95\% \text{ In}_2\text{O}_3 + 5\% \text{ SnO}_2)$ with a thickness of 50 nm were deposited on the *p*-Si(001) boron-doped substrate or Ge thin film by vacuum magnetron sputtering at 125 °C.

AFM measurements were performed with an NT-MDT Ntegra microscope using cantilevers with a tip radius of about 10 nm. Fig. 1a shows the AFM images of the surface consisting of the nanocrystalline Ge film.

The photovoltage temporal dependences were recorded on a Siglent 70-MHz-bandwidth and $1 M\Omega$ input impedance digital oscilloscope with a low-noise amplifier (AD8138) that measured a voltage signal drop across the series load resistance of 47 k Ω (see Fig. 1b).

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Fig. 1. AFM images of ITO-Ge-Si heterojunction surface (a). The scheme for transient photocurrent measurements (b).

3. Results and discussion

Morphology studies showed that low-temperature Ge epitaxy on Si(001) surface at 350° C and high (about 5 nm/min) epitaxy rate leads to formation of nanocrystalline films consisting of Ge crystallites, 5-6 nm in size, which are pseudomorphic to the substrate.

Fig. 2 shows the dark current-voltage (I-V) curves of ITO-Ge-*p*Si and ITO-*p*Si structures at room temperature. The current in the reverse bias is the order of magnitude lower than in forward bias due to the potential barrier of ITO-Si heterojunction.

The shape of curves was analyzed within the framework of the standard diode equation. If the diffusion current and the recombination one are both present in a single diode, the diode model usually describes the dark I-V dependences. The current density J is described as follows:

$$J(V) = J_0 \left(\exp\left(\frac{e(V - IR_s)}{nkT}\right) - 1 \right) + \frac{V - IR_s}{R_{SH}}, \quad (1)$$

where J_0 is the diode reverse saturation current, k - kBoltzmann's constant, T – absolute temperature, R_s and R_{SH} are the series and shunt resistances, respectively. The diode ideality factor is a characteristic of the generation-recombination (G-R) processes, which dominate in the *p-i-n* diodes. They are mainly considered as active only in the space-charge region. It is commonly accepted that n = 1, when the diffusion current dominates, and n = 2, when the recombination current is dominant. Analysis of the forward bias shows that the value $n \approx 3$ within the range from 0.2 to 0.4 V due to significant impact of recombination in the space charge heterojunction and limiting forward current by series resistance. Under U > 0.4 V, the series resistance has a substantial effect on the value of current, which is found to be 193.4 and 204.9 Ω ·cm² at 290 K for ITO-GepSi and ITO-pSi structures, respectively. The inset to Fig. 2 shows the *I-V* dependences measured under AM1.5G illumination. The structure of Ge thin films reveales higher values of short circuit current and photo-EMF in comparsion with the reference ITO-*p*Si structure due to accumulation of a positive charge by Ge NCs and lower values of R_s .

Fig. 3 shows the photovoltage temporal dependences for ITO-Ge-*p*Si and ITO-*p*Si structures measured after excitation by the laser diode with the wavelength 650 nm at different temperatures. Decay curves are approximated by exponential dependence within the investigated temperature range 80 to 290 K:

$$U(t) \sim \exp\left(-t/\tau\right),\tag{2}$$

where τ is a decay constant.

Fig. 4 shows temperature dependences of photovoltage decay constants $\tau(T)$ for ITO-Ge-*p*Si heterojunction and reference ITO-*p*Si structure. The structure with Ge nanostructured thin film reveales faster relaxation of photo-EMF within the temperature range 80 to 290 K. The reason for this behavior is that Ge nanoclusters are additional recombination centers.

The rate of recombination of nonequilibrium carriers involving Ge states determines the value τ for the structure ITO-Ge-*p*Si. The decay constant slightly increases from 28 up to 33 ms under the temperature decrease from 290 down to 220 K. However, the value τ rises with decreasing temperature in the range T < 220 K, which is described as follows:

$$\tau(T) \sim \exp\left(-T/T_0\right),\tag{3}$$

where T_0 is the constant equal to 90.2 K ($kT_0 = 7.8 \text{ meV}$) for structures with Ge nanoclasters.

The observed temperature dependence can be explained by the peculiarities of photogenerated charge carrier transport in a Ge thin film.



Fig. 2. Dark *I-V* curves of the ITO-Ge-*p*Si (1) and ITO-*p*Si (2) structures. The inset shows the *I-V* dependences measured under AM1.5G illumination at 290 K.

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Fig. 3. Time dependences of photovoltage decay for the ITO-Ge-*p*Si (*1*) and ITO-*p*Si (*2*) structures, measured at different temperatures: 85, 155 and 285 K.



Fig. 4. The temperature dependence of photovoltage decay constants for the ITO-Ge-pSi heterojunction and reference ITO-pSi structure.

The charge transport is defined by thermal activation to the band of extended states (multiple trapping) or by hopping via localized states in the film consisting of crystalline Ge NCs of 5...6 nm in size, where the space between them is filled with air and contains amorphous phase of Ge. Under high temperatures, T > 220 K, the recombination rate is determined by times of electron capture/release from traps. When temperature becomes lower, the Ge NCs becomes a giant trap for holes accumulating a positive

charge causing downward band banding in the underlying Si [4, 5]. On the basis of the foregoing, we assume that holes trapped by Ge are practically immobile. Electrons have a chance to meet a hole and recombine only during their transport. In this case, recombination rate depends on the total density of holes and mobility of photoexcited electrons. Under low temperatures, electron transport occurs by hopping within the band of localized states and recombination occurs between hopping electrons and holes trapped by Ge NCs. The number of trapped holes increases under the temperature decrease, while the average jump distance of electrons becomes higher. The photoelectrons will be more and more accumulated in more isolated states with longer release time constants, which will increase τ exponentially with decreasing temperature [6].

4. Conclusions

The obtained results indicate that the Ge film significantly affects the transport and recombination of nonequilibrium carriers in barrier structures based on heterojunction ITO-pSi. The increase in the short circuit current value and photo-EMF in the structure of the Ge thin film barrier is caused by a higher value as compared with the reference ITO-pSi heterojunction. The lifetime of photogenerated carrier is determined by the recombination channel efficiency, which is associated with Ge NCs. The hopping transport of photoexcited electrons in Ge thin films determines the recombination rate in ITO-Ge-pSi heterostructures.

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