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Photocurrent in MIS structures based on germanosilicate films

G.A. Hamoud [1, 2] ✉, G.N. Kamaev [1, 2], M. Vergnat [3], V.A. Volodin [1, 2] ✉

[1] Rzhanov Institute of Semiconductor Physics, Siberian Branch of RAS, Novosibirsk, Russia;
[2] Novosibirsk State University, Novosibirsk, Russia;
[3] Université de Lorraine, Nancy, France
✉ k.gaisaa@g.nsu.ru, ✉ volodin@isp.nsc.ru

Abstract. The photocurrent in metal-insulator-semiconductor (MIS) structures based on germanosilicate films on n-type silicon with a transparent top electrode made of indium tin oxide has been studied. The first structure contained a $GeO[SiO_2]$ layer as a dielectric, and the second structure contained an additional Ge layer 3 nm thick, separated from the silicon substrate by a tunnel-thin layer of SiO_2. High photosensitivity was obtained for both structures, both as-deposited and after annealing at 500 °C for 30 minutes. A mechanism for the generation of photocurrent is proposed, based on the absorption of photons in a depletion region of silicon and tunneling of charge carriers through the dielectric. In the case of the second structure, an additional mechanism for the occurrence of photocurrent associated with the absorption of photons in the Ge layer is assumed. The studied MIS structures can be used in simple, inexpensive photodiodes that do not require the creation of *p–n* junctions.

Keywords: germanosilicate films, MIS-structures, photocurrent

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Фототок в МДП-структурах на основе германосиликатных плёнок

Г.А. Хамуд [1, 2] ✉, Г.Н. Камаев [1, 2], М. Вернья [3], В.А. Володин [1, 2] ✉

[1] Новосибирский государственный университет, г. Новосибирск, Россия
[2] Институт физики полупроводников им. А.В. Ржанова Сибирского отделения РАН, г. Новосибирск, Россия
[3] Университет Лотарингии, г. Нанси, Франция
✉ k.gaisaa@g.nsu.ru, ✉ volodin@isp.nsc.ru

Аннотация. Исследован фототок в структурах металл-диэлектрик-полупроводник (МДП) на основе германосиликатных плёнок на кремнии n-типа с прозрачным верхним электродом из оксида индия и олова. Первая структура содержала в качестве диэлектрика слой $GeO[SiO_2]$, а вторая содержала ещё слой Ge толщиной 3 нм, отделённый от подложки кремния туннельно-тонким слоем SiO_2. Получена высокая фоточувствительность обеих структур, как исходных так и после отжига 500 °C, 30 минут. Предложен механизм возникновения фототока, основанный на поглощении фотонов в обеднённом слое кремния и туннелировании носителей заряда через диэлектрик. В случае второй структуры предположен дополнительный механизм возникновения фототока, связанный с поглощением фотонов в слое Ge. Исследованные МДП-структуры можно использовать в простых, недорогих фотодиодах, не требующих создания *p*–*n*-переходов.

Ключевые слова: германосиликатные пленки, МДП-структуры, фототок

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Introduction

In recent years, there has been increasing interest in the use of metal-insulator-semiconductor (MIS) structures in photovoltaics. Typically, in MIS photodiodes and optical detectors, tunnel or thick layers of SiO_x are used as a dielectric [1]. To improve photosensitivity, Ge quantum dots were included in SiO_x layers [2]. Germanosilicate films ($GeSi_xO_y$) have some advantages over SiO_x. The purpose of this work is to study the photocurrent effect in MIS structures based on $GeSi_xO_y$ (including those with Ge inclusions).

Materials and Methods

High-vacuum electron beam vapor deposition technique was employed to deposit the non-stoichiometric germanosilicate glass layers $GeSi_xO_y$, on *n*-Si (100) substrates (specific conductivity $\rho = 5.5 \pm 1$ Ohm·cm) at room temperature. The targets were evaporated and co-evaporated in a vacuum of about 10^{-7}–10^{-6} Torr, and using a quartz microbalance, the deposition rate was maintained within a range of about angstroms per second. The targets were powders of various materials, such as GeO_2, SiO_2, and Ge. It is known that when germanium dioxide powder evaporates the $GeO_{1.1-1.2}$ films are deposited [3]. More details are provided about the growth conditions and stoichiometry of the deposited films in [3].

In order to explain the mechanism of photocurrent appearance in the $GeSi_xO_y$ based MIS-structures, it is important to know where the light is absorbed in the substrate or in the films. To clarify this, the $GeSi_xO_y$ films and many-layer structures were deposited on special satellite substrates - glass coated with a special transparent conductive fluorine-tin-oxide (FTO). Since the top electrode of the MIS structures was made of ITO, it was important to know how transparent it was. So, a layer of transparent indium-tin-oxide (ITO) was also deposited on a transparent sapphire substrate without a mask, and then the reflection and transmission spectra of all samples were measured separately using an SF-56 spectrophotometer (produced by LOMO-Spectr, Russia), with a spectral resolution of 2 nm and the measuring range from 190 to 1100 nm. A special PS-9 setup was employed to register the reflection spectra, that have a reflectance with an incidence angle close to the normal of about 9°. The recorded spectrum was then normalized to the spectrum of silicon with a natural oxide with thickness of 2.5 nm as the reference spectrum.

Fig. 1, *a*, c shows the schematic structure of the samples. The $GeO[SiO_2]$ layers were obtained by co-evaporation for target powders (GeO_2 and SiO_2). As for the ITO top electrodes, they were deposited using special mask and magnetron sputtering. The thickness of ITO was 200 nm with a surface resistance of about 40 Ohm/□, an area of top electrodes was 0.49 mm^2. Both as-deposited and annealed MIS-structures were studied. The time of annealing was 30 minutes at a temperature of 500 °C in atmospheric air. The *I*–*V* characteristics were studied before and after annealing using an Agilent B2902A parameter analyzer, the bottom electrodes were a silicon substrate with indium-gallium paste that was grounded during the experiment and the top electrodes was the ITO contacts to which positive and negative voltages were applied. Moreover, the *I–V* characteristics were studied in the dark and under illumination of a halogen lamp. The light spot was focused on one of the ITO top electrode. The size of the spot was about 1 mm^2. The optical power density was about 1000 Watts per square meter, so about 0.5 milliwatts fell on the top electrode area.

Results and Discussion

Fig. 1, *a*, *b*, *c*, *d* shows the *I–V* characteristics in the dark and when illuminated with a halogen lamp for samples 1 (without Ge inclusion) and 2 (with 3 nm thick Ge layer) before and after annealing. As one can see from dark *I–V* characteristics of all as-deposited and annealed samples, they all have diode characteristics. It is also clear for all samples that photocurrent occurs especially with reverse bias. Next, we consider the effect of annealing on the *I–V* characteristics for both samples.

For the structure of the as-deposited sample 1 (without Ge inclusion), one can see that with the reverse bias the dark current is relatively large (Fig. 1, *a*), photocurrent exceeds dark current by 2–3 times. As seen from Fig. 1, *b*, the annealing leads to notable reduction of dark current and to slight decrease of light current. Presumably, after annealing, the properties of the MIS structure change, due to formation of amorphous germanium nanoclusters in GeO[SiO_2] layer during annealing, which alter the transport properties of $GeSi_xO_y$ films [3]. It is worth noting that the light current exceeds the dark current by about four orders of magnitude under reverse bias and that there is a significant light current under direct bias (Fig. 1, *b*).

As for the *I–V* characteristics of sample 2 (before annealing, with Ge inclusion), Fig. 1, *c* shows good diode characteristics and relatively high photocurrent under the negative (reverse) bias. Some hysteresis is also seen in light *I–V* characteristics, which can be associated with charging of the germanium layer. Evidently, annealing also led to modification of the *I–V* characteristics (Fig. 1, *d*). It can be observed from the dark *I–V* characteristics that the current minimum is

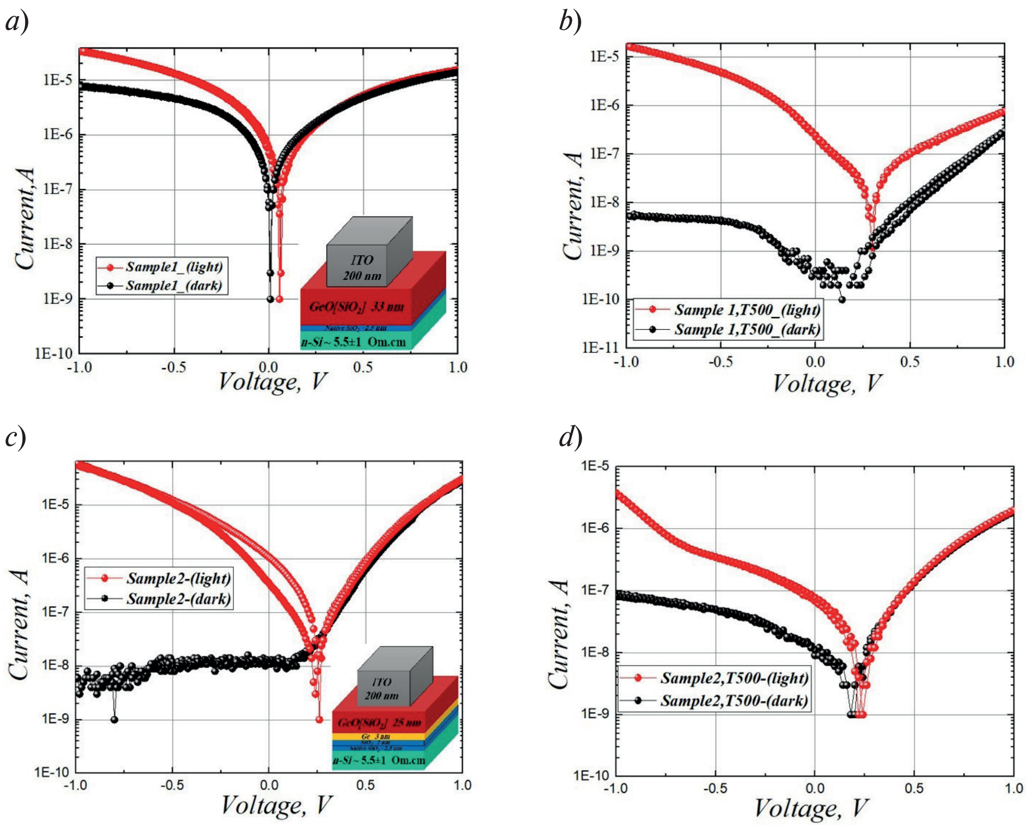

Fig. 1. *I–V* characteristics (dark marked by black circles and light by red circles) of MIS structures: sample 1 without annealing (*a*); sample 1 after annealing (*b*); sample 2 without annealing (*c*); sample 2 after annealing (*d*)

not observed at zero voltage bias. This is due to the effect assumed above, i.e., charging of the germanium layer. Notice that annealing of this sample did not improve photosensitivity, as the difference between the ratio of light current to dark current decreased (Fig. 1, *c* and 1, *d*), in contrast to sample 1, where the annealing leads to improving of photosensitivity. However, as already noted, as-deposited sample 2 has very good photosensitivity.

To find out where the light is absorbed (in the ITO contacts, in the $GeSi_xO_y$ films, or in the silicon substrate), we studied the reflection and transmission spectra of: ITO contacts on transparent sapphire substrates; glass with FTO; sample 1 deposited on glass with FTO; the sample 2 deposited on a glass substrate with FTO. It was obtained from the analysis of the transmission and reflection spectra of the ITO film on sapphire (the spectra are not shown here) that the ITO top electrodes are practically transparent to light in the range from 400 nm to 800 nm and showed no absorption of light in this range. For the glass with FTO, as Fig. 2, *a* shows, the sum of the transmission spectrum with reflection spectrum in the range of green light (wavelength ~ 500 nm) is about 85% (Fig. 2, *a*). The same value was obtained for sample 1 deposited on the glass with FTO (Fig. 2, *b*). This means that the $GeO[SiO_2]$ film in this sample does not absorb light and most of the light is absorbed in the Si substrate (in the case of MIS-structure). But for sample 2 deposited on the glass with FTO, the sum of reflection and transmittance is about 70% (Fig. 2, *c*). This leads us to the conclusion that ~ 15% of the light falling on sample 2 is absorbed in the multilayered structure, especially in the germanium layer, and the rest of the light is absorbed in the Si substrate (in the case of MIS-structure). It is worth noting that although the maximum spectral power of a halogen lamp is in the red range, there is a noticeable amount of green and blue light in its spectrum.

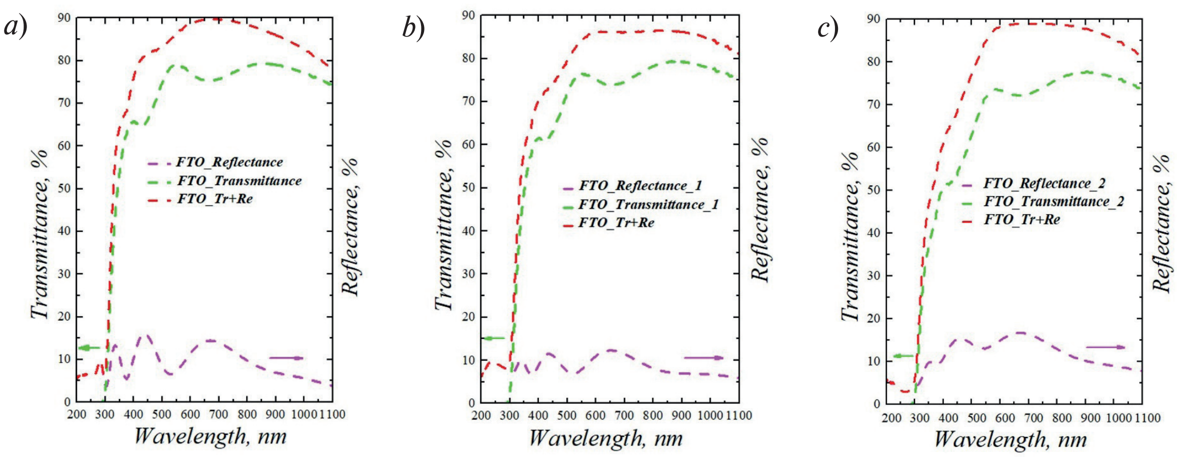

Fig. 2. Transmittance, reflectance spectra, and its sum: FTO film on a glass substrate (*a*); sample 1 on a glass substrate with FTO (*b*); sample 2 on a glass substrate with FTO (*c*)

Now we can conclude that most of the light is absorbed in the Si substrate for both MIS-structures (samples 1 and 2), but part of the light is absorbed in the germanium layer for the second MIS-structure (sample 2). Both mechanisms of photocurrent appearance are shown in Fig. 3. The mechanism that occurs here is analogous to the photocurrent mechanism that happens in solar cells with Schottky barriers [4]. For the first sample, the reverse bias creates a large region of space charge, namely, the depletion region, which can be estimated based on the known relationship of the Irwin curves for silicon. According to Irwin curves, the donor concentration corresponding to the value of the resistivity of 5.5 ± 1 Ohm·cm is 10^{15} cm^{-3}. Therefore, the width of the depletion region at half a volt is 0.8 micrometers and increases with increasing voltage value, reaching 3.2 micrometers at -8 V. This region absorbs the incident photons, which generate the electron-hole pairs that contribute to increasing the photocurrent. The photoelectrons drift to the bottom electrode due to reverse bias. The photoholes drift to the native-SiO_2/$GeO[SiO_2]$ (sample 1) or to the SiO_2/Ge/$GeO[SiO_2]$ multilayered structure (sample 2). It is important to note here that the silicon dioxide layer between the silicon substrate and the $GeO[SiO_2]$ film (sample 1) or the Ge/$GeO[SiO_2]$ multilayered structure (sample 2) is tunnel thin, as in the case of Ge quantum-dot-based photodetector [2]. So, photoholes can tunnel through it. There are then two possible paths for photoholes. They can move through the traps to reach the ITO top electrode (blue path, Fig. 3) or they can recombine in the GeO[SiO_2] film (sample 1) or in the Ge layer (sample 2) with electrons, which can drift from ITO top electrode due to reverse bias.

For the sample 2, there is an additional mechanism where some of the light is absorbed in the germanium layer and an electron-hole pair is generated in this layer. Electrons can pass easily (due to tunneling) through the insulating layer (SiO_2 ~ 4.5 nm) since the Ge/Si is a type II heterostructure, so the energy level for electrons in Ge is higher than the energy level for electrons in Si. But for the photoholes, the Ge layer is quite a deep trap. Also here, the photoelectrons can pass through the circuit as in the previous mechanism. While for holes, they either can move through the traps to reach the ITO contacts and recombine with the electrons injected from them, or they can recombine with the electrons which can drift through the traps from the ITO top electrode.

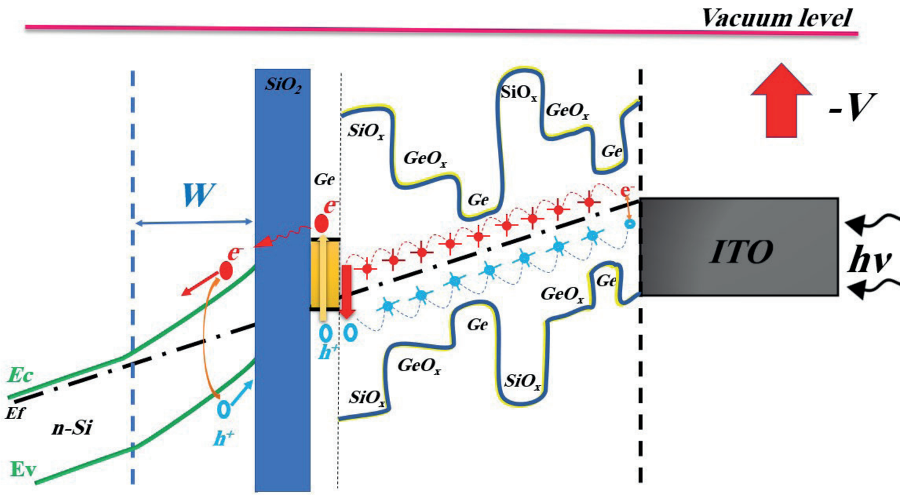

Fig. 3. Mechanism of photocurrent occurrence in the sample with and without a Ge layer

Conclusion

1) The possibility of using $GeSi_xO_y$ films in photosensors has been demonstrated, and a good ratio of photocurrent to dark current (photosensitivity) has been obtained. The annealing has improved this ratio for the sample without a Ge layer, as this photosensitivity reached 4000 at the -1 V bias, and worsened it for the sample with a Ge layer, as the photosensitivity at the -1 V bias decreased from 6250 to 50. We point out that our photosensitivity is much better than the optical sensitivity obtained in work [2] using quantum dots of germanium.

2) The use of a MIS structure including Ge layers can presumably make it possible to expand the sensitivity edge of photodetectors to the long-wavelength region.

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THE AUTHORS

HAMOUD Ghaithaa A.
k.gaisaa@g.nsu.ru
ORCID: 0009-0001-6796-4432

KAMAEV Gennadiy N.
kamaev@isp.nsc.ru
ORCID: 0000-0002-6413-0969

VERGNAT Michel
michel.vergnat@univ-lorraine.fr
ORCID: 0000-0001-5237-9014

VOLODIN Vladimir A.
volodin@isp.nsc.ru
ORCID: 0000-0002-1431-8242

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