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STUDY OF Ge NANOPARTICLES EMBEDDED IN AN AMORPHOUS SiO_2 MATRIX WITH PHOTOCONDUCTIVE PROPERTIES

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Electrical and photoconductive properties of films consisting of amorphous Ge nanoparticles uniformly distributed in amorphous SiO_2 were studied. These films were prepared by sol-gel method and treated by rapid thermal annealing technique. Measurements of current-voltage and conductance-temperature characteristics, spectral and bias dependences of the photocurrent on samples with coplanar geometry of electrodes, were performed. The current-voltage characteristics have a weak rectifying behaviour. The variable range hopping transport mechanism, described by the Mott law, in amorphous materials, in the absence of dominant Coulomb interactions, was evidenced in the temperature dependence of the dark current. The samples exhibit very good photoconductive properties, explained by taking into account the Ge clusters and defects, produced by the rapid thermal annealing.

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1. Introduction

Ge nanodots have received a considerable interest in recent years because of their potential applications in nano-optoelectronics (high performance photodetection and light emitting devices), memory devices and sensors.

Ge nanocrystals embedded in SiO_2 matrix exhibit photoluminescence (PL) [1, 2] which is attributed to the interface traps between Ge quantum dots and the SiO_2 matrix or to the quantum confinement effects.

The sol-gel method is attractive for preparation of films formed by Ge nanoparticles embedded in SiO_2 matrix, due to its technological advantages. The sol–gel films contain a relatively low Ge concentration with respect to Si, and Ge nanoparticles are rather small [3]. The sol-gel technique starting from now conventionally used tetraethyl orthosilicate $Si(OC_2H_5)_4$ (TEOS) and $GeCl_4$ was reported for the first time by Nogami and Abe in 1994 [1]. The annealing procedure was carried out at 400 – 800 °C under a flowing 20 % H_2 – 80 % N_2 mixed gas. The films contained 7 wt % Ge. They reported PL from Ge nanocrystals with average size of 5 – 7 nm, evidenced in a broad but pronounced PL spectrum, for samples annealed at 700 ^oC. In films annealed at 800 ^oC, larger Ge nanocrystals were found, and PL was not observed.

Yang et al [2] showed that PL arises from the very small Ge clusters (with diameters smaller than 1 – 2 nm) in sol-gel films with Ge/Si ratio of 15 % in mixed sols. The annealing of films at 500 – 700 ^oC under a flowing H_2 gas was performed. The strongest PL was observed in films annealed at 500 ^oC. The authors showed that very small Ge clusters are present in these samples. When the annealing temperature increases, the most part of Ge crystallizes in nanoparticles, while the fraction of Ge clusters decreases, so that a decrease in the PL intensity is observed.

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There are few studies in the literature focused on the electrical and photoelectrical phenomena in films of Ge nanoparticles embedded in SiO_2 matrix, especially in sol-gel films. Yang et al [4] showed that if Ge concentration is sufficiently large, the electrical conduction is good. They suggested several alternative conduction mechanisms such as hopping mechanism, direct tunneling and Fowler-Nordheim tunneling, in Ge-implanted SiO_2 thin films. The Fowler-Nordheim tunneling was also observed in a multilayer structure fabricated by ion beam sputtering deposition [5]. For RF magnetron sputtered films without annealing, a variable range hopping (VRH) mechanism, characterized by a temperature dependence of conductance as $\ln G \propto T^{-1/4}$, through localized states associated with Ge clusters was proposed [6]. For films annealed at 800 ^{o}C, containing Ge nanocrystals with average diameters between 3.8 and 8.9 nm, a $\ln G \propto T^{-1/2}$ dependence was found [7]. The authors explained the electrical transport as taking place through Ge nanocrystals by tunnelling between neighbouring ones.

Tzeng and Li [8] reported an enhanced 400 – 600 nm photoresponsivity of metal-oxide-semiconductor photodiodes with Ge quantum dots in the gate oxide. They attributed this effect to the quantum confinement effect in Ge quantum dots. This effect is controlled by trapped holes in Ge quantum dots. Castrucci et al [9] showed that layers of Ge nanodots deposited by molecular beam epitaxy on a thin amorphous SiO_2 film, thermally grown on Si (100) substrates are photoconductive in the visible and ultraviolet range.

In this paper we present electrical and photoelectrical investigations made on structures prepared by the sol-gel method and annealed by a rapid thermal annealing (RTA) technique. These films are formed from Ge nanoparticles dispersed in amorphous SiO_2 matrix (GeSiO). Current-voltage ($I - V$) and conductance-temperature characteristics, spectral dependence of photocurrent and photocurrent dependence on voltage curves were measured. We present the measurements and examine the results. Our films present very good photoconductive properties.

2. Experimental

The films investigated in this paper, consisting of Ge nanoparticles embedded in an amorphous SiO_2 matrix, were prepared by sol-gel method. As precursors, we used $GeCl_4$ and TEOS, and as a solvent, ethanol. The sols of GeO_2 and SiO_2 were mixed for Ge/Si molar ratio of 3 %, and then the final mixture was stirred for 2 – 4 h. The oxide layer was deposited by spin coating method on a silicon substrate, followed by a subsequent drying and heating in air at 500 – 600 ^{o}C. Thus, compact and homogeneous films were prepared. After the deposition, these films were annealed in N_2 atmosphere, at 800 – 950 ^{o}C, by RTA for 5 – 15 min, to allow Ge nanoparticles formation. In order to perform electrical and photoconductivity measurements, Al electrodes were deposited at 2 mm distance from each other, in a coplanar geometry.

The samples were mounted in a Janis CCS-450 cryostat (10 – 500 K). The electrical and photoconductivity measurements were performed on a computer-assisted set-up controlled by LabVIEW 8.5.1, consisting of Keithley 6517A electrometer, Stanford SR 830 double lock-in amplifier, Newport monochromator, Newport light source 1000 W (Xe) (UV-VIS-NIR), LakeShore 331 Temperature controller and Stanford SR 540 chopper.

3. Results and discussion

Transmission electron microscopy (TEM) investigations revealed that the films with a thickness of 250 – 280 nm are formed from Ge-rich nanoparticles with sizes in the range of 2 – 10 nm, almost uniformly distributed in the amorphous SiO_2 matrix (see Fig. 1). These results are similar with those obtained in Ref. [3]. At the interface with the Si substrate, the GeSiO films present a clear SiO_2 matrix of about 10 nm in width, without nanoparticles. At the limit between this clear band and the rest of the film there are larger nanoparticles with a higher density in comparison with that found in the film (see Fig. 1 left). The TEM images presented in Fig. 1 shows that the most of the Ge nanoparticles are amorphous. However, some of them present small areas with lattice fringes like contrast with a periodicity of about 0.37 nm (see Fig. 1 right), suggesting the presence of ordered Ge clusters close to Ge tetragonal phase, as we observed in a previous paper [3]. In these sol-gel films, Ge clusters are produced during the RTA treatment.

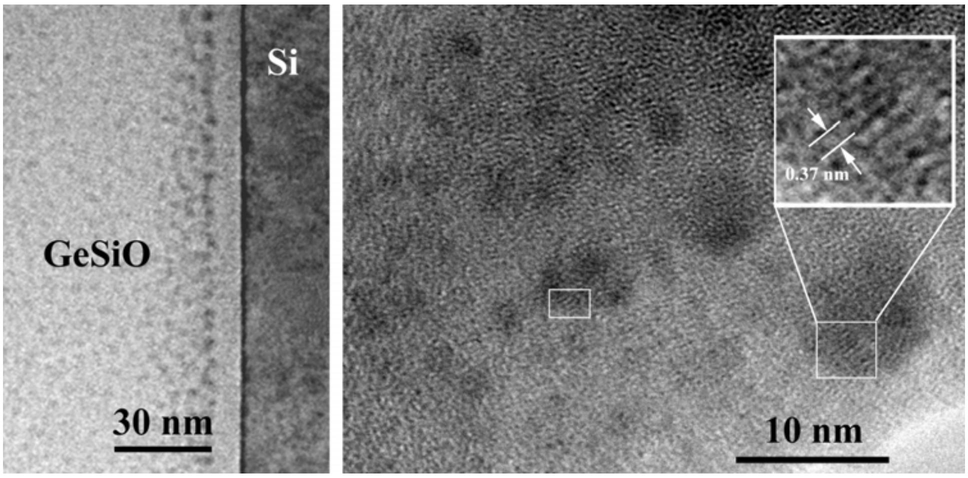

Fig. 1. TEM images of the GeSiO film with 3 % Ge. Morphology of the interface between the Si substrate and the GeSiO sol-gel film (left); lattice fringes like contrast visible in some of globular amorphous nanoparticles embedded in SiO_2, shown in the square frames (right).

The current – voltage characteristic taken at room temperature (RT), in the interval 0 – 1 V, for both bias polarities, is presented in Fig 2. This curve is asymmetric and it suggests a weak rectifying behaviour. For a bias higher than 0.4 V the curve becomes linear.

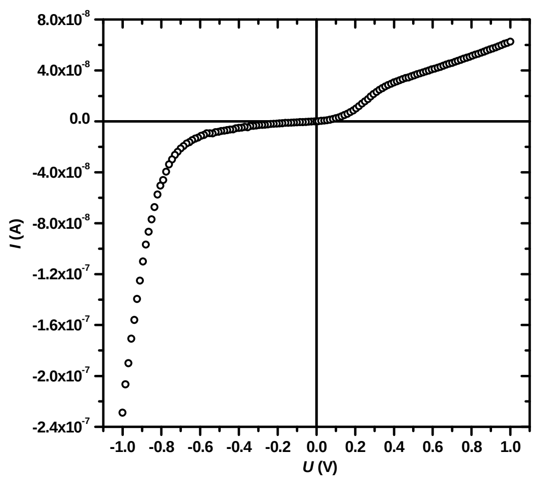

Fig. 2. I – V characteristic measured at RT.

The weak rectifying behaviour observed in the current-voltage characteristics is mainly given by the junction formed between GeSiO film and Si substrate. The Ge nanoparticles with higher density, located at the interface SiO_2 clear band / GeSiO film, induce a depletion layer in the Si substrate. The linear dependence of $I – V$ characteristics for positive bias, higher than 0.4 V, shows that this behaviour is dominated by the series resistance of the film. Similar results were obtained by Ray et al [10] on a similar structure containing porous silicon instead of GeSiO film. Therefore, the experimental curve from Fig. 2 was fitted with the equation:

$$I = I_S \exp\left(\frac{q(V - I \times R_S)}{nkT}\right)\left[1 - \exp\left(\frac{-q(V - I \times R_S)}{kT}\right)\right], \quad (1)$$

which takes into consideration the effects of thermionic emission (on reversed polarity) and electron-hole recombination in the depletion region between the silicon wafer and the GeSiO film. I_S represents the reverse current at 0 V bias, q is the electron charge, n is the ideality factor, and R_S is an appropriate series resistance. In our case one obtains I_S = 39 pA, n = 1.30, and R_S = 0.2 MΩ. The $I - V$ characteristic associated with Eq. 1 fits well the experimental data, as one can see in Fig 3. For voltages higher than 0.4 V the contribution of the film dominates, so that the $I - V$ curve becomes linear.

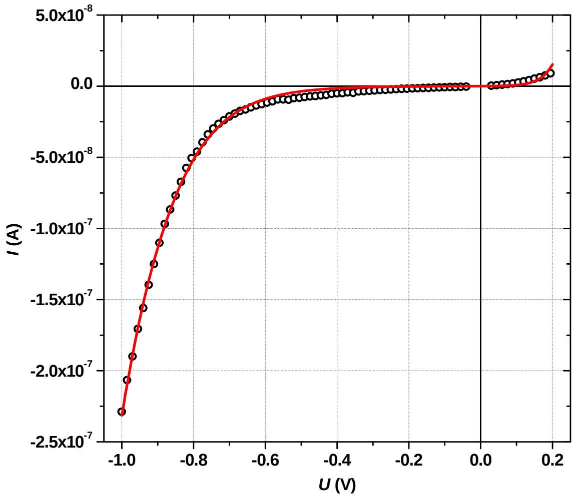

Fig. 3. Dark current-voltage characteristic: open circles – experimental and continuous line – fit curve.

The curves representing the temperature dependence of the conductance were fitted with different functions corresponding to different possible transport mechanisms. The best fit on the whole temperature interval used for measurements was obtained for the Mott law $I \propto \exp\left[-(T_0/T)^{1/4}\right]$ that describes the VRH transport mechanism in amorphous materials, in the absence of dominant Coulomb interactions. A typical characteristic of the temperature dependence of the conductance G measured for a bias of 0.9 V is shown in Fig. 4. Similar behaviour is obtained for 0.5 and 0.8 V. In our opinion, the VRH transport takes place on localized states in amorphous GeSiO films including those associated with Ge clusters [6].

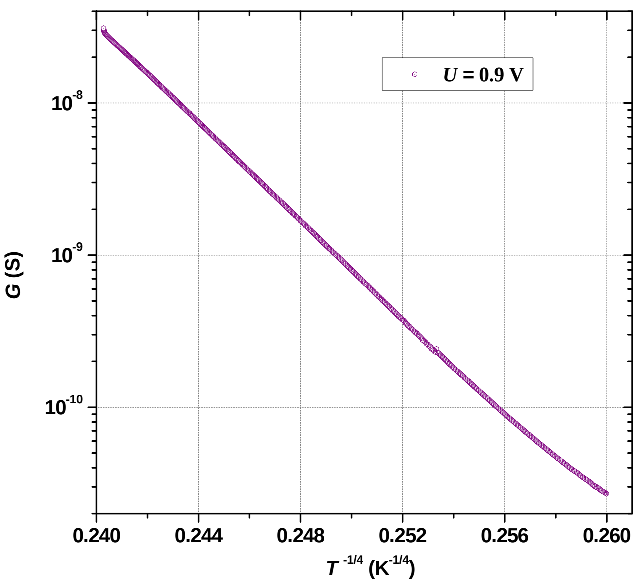

Fig. 4. Conductance– temperature characteristic.

These films exhibit very good photoconductive properties. For example, if the sample is illuminated with white light from an incandescence lamp of 40 W, the photocurrent is with 2 – 3 orders of magnitude larger than the dark current. In Figs. 5a) and 5b) we present the spectral dependence of the photocurrent (I_f) measured at RT in the 350 – 900 nm wavelength range, for different constant biases in the 0 – 1 V interval. In Fig. 5a) I_f curves not normalized to the incident light intensity are shown, while Fig. 5b) illustrates the normalized ones. The measurements were performed using modulated light, with an 80 Hz chopping frequency. As one can see, the curves present a fine structure with five main maxima located at 513, 724, 773, 804 and 862 nm, respectively.

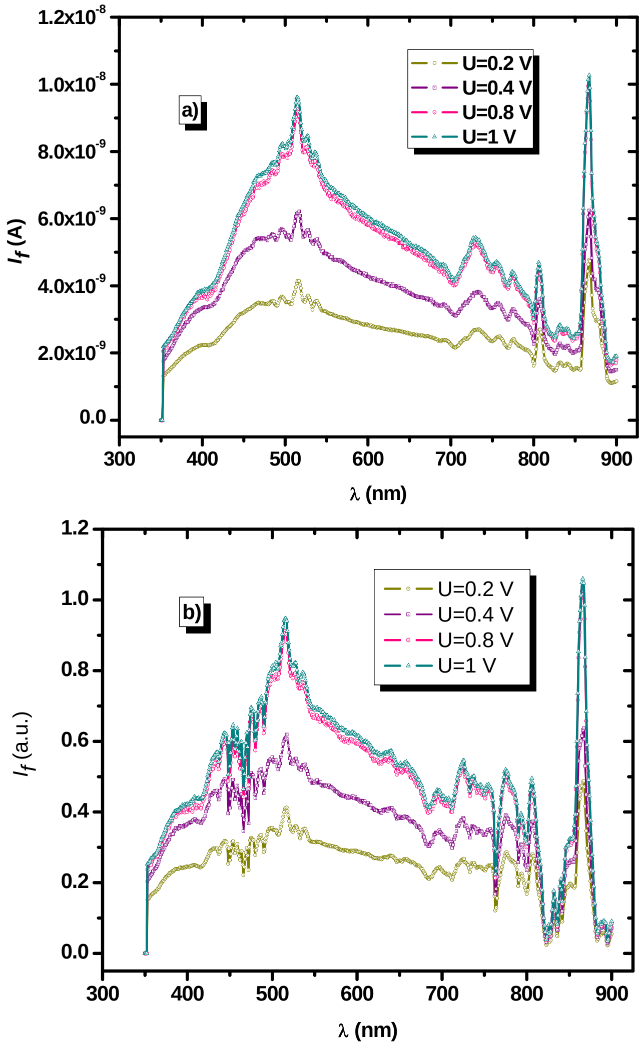

Fig. 5. Spectral dependence of the photocurrent measured at 0.2, 0.4, 0.8 and 1 V: a) not normalized and b) normalized to the incident light intensity.

The photocurrent-voltage (I_f – V) characteristics for different wavelengths corresponding to the main maxima from Fig. 5b) are given in Fig. 6. For these measurements the sample was excited with continuous monochromatic light and the curves were not normalized to the incident light intensity as those from Fig. 5a). The dark current-voltage characteristic is also presented in Fig. 6 for comparison. One can see that the photocurrent at 1 V for the sample illumination corresponding to the maximum located at 862 nm is larger with about two orders of magnitude than the dark current at the same voltage. This proves very good photoconductive properties of the films.

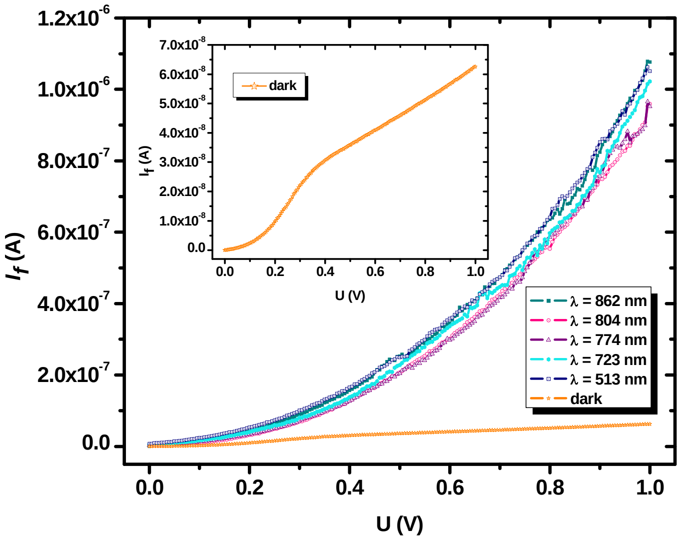

Fig. 6. The I_f – V characteristics for sample illuminated with monochromatic light of wavelengths corresponding to the photocurrent maxima in Fig. 5b). The dark current-voltage curve is given for comparison.

The high photoconductivity could be given by the light absorption on both Ge clusters [2] and defects (localized states) associated with Ge clusters. The defects produced by RTA can also act as traps: if carriers of one type, let us say holes, are trapped, the lifetime of electrons is increased and they will participate in the photoconductivity. The fine structure of the spectral curves is also influenced by the localized states / defects present in the films. We have to remark that the other sol-gel films which we annealed in a heater at the same temperature and atmosphere do not show high photoconductivity as those annealed by RTA.

4. Conclusions

In this paper, the electrical and photoconductive properties of films consisting of amorphous Ge nanoparticles uniformly distributed in amorphous SiO_2 prepared by the sol-gel method and annealed by RTA technique were studied. The weak rectifying behaviour of samples with coplanar geometry of electrodes is mainly given by the junction between GeSiO film and Si substrate. The variable range hopping transport mechanism in amorphous semiconductors ($\ln G \propto T^{-1/4}$) was evidenced.

The investigated films have very good photoconductive properties, induced by the rapid thermal annealing. The spectral distribution of the photocurrent presents five main maxima. The photocurrent value for a bias of 1V is about two orders of magnitude larger than the dark current value at the same bias, even the film is excited with monochromatic light. The high photoconductivity of our films is mainly due to the light absorption on Ge clusters and defects (localized states) and to trapping centres. These defects appear during the rapid thermal annealing treatment.

These films represent a promising material for solar cells based on nanostructures consisting of Ge nanoparticles embedded in SiO_2 matrix.

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