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Electrical and Optical Properties of SiO_2 Thin Layers Implanted with Zn Ions

K. Czarnacka[a,*], T.N. Koltunowicz[b], M. Makhavikou[c], I. Parkhomenko[c] and F.F. Komarov[c]

[a]University of Life Sciences in Lublin, Akademicka 13, 20-950, Lublin, Poland
[b]Lublin University of Technology, Nadbystrzycka 38d, 20-618, Lublin, Poland
[c]Belarusian State University, 4, Praspyekt Nyezalyezhnastsi, Minsk, Belarus

This paper presents the results of electrical and optical measurements of 600 nm thick silicon dioxide on Si layers to which zinc ions have been implanted. Following ion implantation the samples were annealed in air at 1023 K for 2 h. For the samples immediately after preparation and being annealed, AC measurements of resistivity R_p, phase angle θ , capacity C_p, and dielectric loss factor tanδ were made as a function of frequency (measurement range 50 Hz–5 MHz) and the measurement temperature (20 K–375 K). On this basis, the frequency–temperature dependence of conductivity σ was prepared. The strong frequency dependence of conductivity indicates that in the Zn/SiO_2 layer after annealing, the conductivity takes place by hopping exchange (tunneling) of electrons between nanoparticles of the Zn metallic phase or between ZnO. Moreover, there is a clear change in the nature of conductivity at high frequencies. The photoluminescence spectra of the as-implanted Zn-SiO_2-nanocomposites exhibit a blue-green band. This band is caused by the formation of oxygen vacancies in silicon dioxide. The intensity of this peak is observed to grow with the increasing annealing temperature. Besides, a strong orange-red band was revealed in the photoluminescence spectra of the annealed sample. This emission may be attributed to the presence of oxygen interstitial/antisites. The effect of thermal annealing on light-emitting properties has been discussed.

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1. Introduction

The preparation of metal and/or semiconductor nanostructures embedded in the dielectric matrices is one of the hot research topics due to their unique structure and new interesting properties such as special optical, electrical, and magnetic properties, which depend on the size etc. [1, 2]. The thermally obtained silicon dioxide SiO_2 is a very important material in the electronic industry where it is widely used as a high quality insulator. The addition of metallic or semiconductor nanoparticles to the SiO_2 matrix enabled rebuilding of the electronic structure and physical properties of this material with a wide band gap-approximately 9 eV.

One of the best-adapted and pure techniques for obtaining nanoparticles in a dielectric matrix is ion implantation and ion sputtering [3–5]. In this way it is possible to obtain nanocomposites exhibiting phenomena of electron tunneling [6] or non-coil inductance [7, 8]. Moreover, the ion implantation into metal alloys affects their strength and corrosion properties [9, 10].

The purpose of the paper was to obtain a thin layer consisting of silicon dioxide into which zinc ions were implanted. Annealing enabled to obtain a nanocomposite of a dielectric matrix of silica (SiO_2) with ZnO semiconductor nanoparticles. Photoluminescence (PL) and AC electrical measurements of the obtained layers were performed allowing determination of the structure and nature of conduction.

2. Experimental

The object of the research was a layer of thermally obtained silicon dioxide with a thickness of 600 nm to which zinc ions with energy 130 keV and fluence 1×10^{17} ion cm^{-2} were implanted. The ion implantation process was performed at room temperature. Afterwards the samples were annealed at 750 °C in air atmosphere for 120 min.

PL spectra were recorded at room temperature in the spectral range of 350–800 nm with a He–Cd laser (3.8 eV) as an excitation source using a home-made setup.

Measurements of electrical parameters of the obtained material before and after annealing were made using the measuring station described in the paper [11]. The main measurement parameter was resistance R_p as a function of frequency (50–5 $\times$ 10^6 Hz) and temperatures in the range 20–375 K. The other AC parameters such as capacity C_p, phase angle θ, and the tangent of the dielectric loss angle tan δ were also measured. Referring to the geometrical dimensions of the sample and the measured resistance, the frequency–temperature dependence of the conductivity σ of the examined material

*corresponding author; e-mail: karolina.czarnacka@up.lublin.pl

was determined. On this basis, the Arrhenius conductivity diagrams were developed and the electron activation energies were calculated.

3. Results and discussion

Figure 1 shows the room-temperature PL spectra of the as-implanted SiO_2/Si samples annealed at 750 °C for 120 min. The as-implanted sample exhibits a weak visible emission with the maximum in the blue spectral range (∼ 2.8 eV). The annealing results in an increase of PL intensity. Besides, the PL spectra of annealed sample can be deconvoluted by the three Gaussian bands. The dominant emission band is located at 2.07 eV (600 nm) in the orange region. The second intensive blue band was centered at 2.64 eV (470 nm). Also the weak UV emission band at 3.28 eV (378 nm) is found in the PL spectra of the annealed sample.

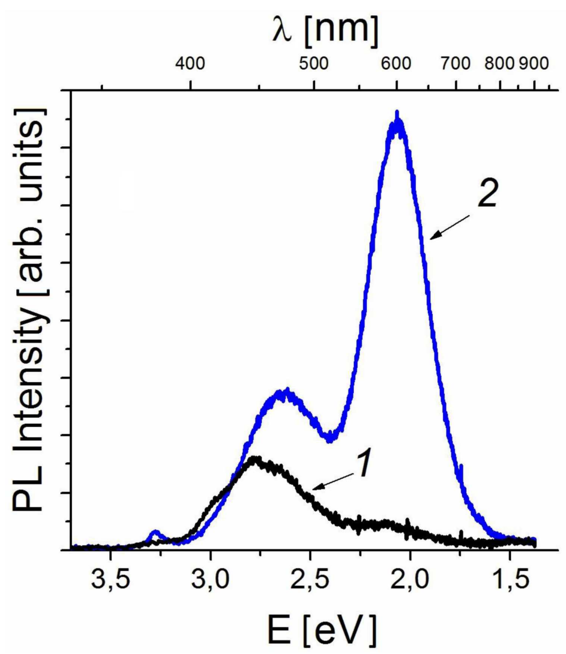

Fig. 1. PL spectra of as-implanted (1) and annealed (750 °C, 120 min) samples.

It was assumed that the weak emission of as-implanted samples could be attributed to radiative recombination via defects in the silica matrix introduced during implantation (for example, Zn-related oxygen deficient centers) [12]. The increase of PL intensity via annealing can be explained by formation of ZnO phase. Namely, the weak UV band can be attributed to the near band edge emission of ZnO nanostructures attributed to the free exciton recombination which has been reported elsewhere [13, 14]. The weak intensity of near band edge emission can be explained by the presence of defects in the synthesized nanoclusters. On the other hand, the strong emission in the blue and orange spectral ranges can be related to the deep level emission resulting from the native defects in ZnO. Namely, the blue band can be originated by electron transition from the extended states of interstitial Zn (Zn_i) to the valence band [14]. The orange band can be attributed to surface disordered ZnO nanostructures and zinc vacancies and/or interstitial oxygen in ZnO [13–15].

As a result of AC measurements, the frequency–temperature dependence of conductivity σ was obtained. Figure 2 shows such dependence for the material annealed in air for 120 min at a temperature of 750 °C. There is a clear increase in conductivity with frequency. According to Mott [16], such behaviour is indicative of the hopping mechanism of charge transport. What is more, in the frequency range up to about 10^6 Hz, there is a noticeable increase in the conductivity with a measuring temperature that confirms the dielectric nature of the conduction. At high frequencies this mechanism changes. It can be seen that the conductivity decreases slightly with the temperature of measurement which corresponds to the metallic type of conduction.

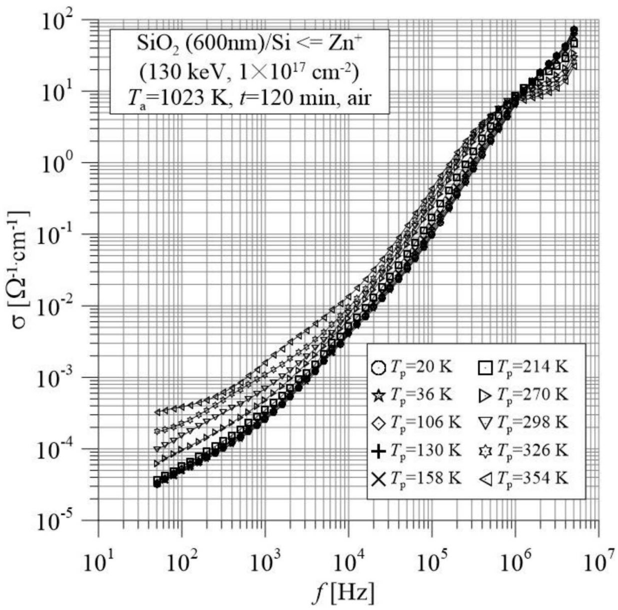

Fig. 2. Frequency–temperature dependence of conductivity σ of nanocomposite Zn–SiO_2 annealed at temperature $T_a = 750$ °C for $t = 120$ min.

The Arrhenius conductivity graphs determined for the two measurement frequency values — 10^4 Hz (Fig. 3) and 3.98×10^6 Hz (Fig. 4) — show these changes very well. At lower frequencies there are three ranges of changes in the activation energy, which correspond to the minimum of two types of nanoparticles in the SiO_2 matrix–Zn and ZnO nanoparticles, as photoluminescence studies have shown. The first one is at the temperatures 20–60 K where the activation energy is $\Delta E_1 \approx$-0.0001 eV. Here conductivity decreases slightly with the temperature and so there is a metallic type of conduction and therefore the activation energy

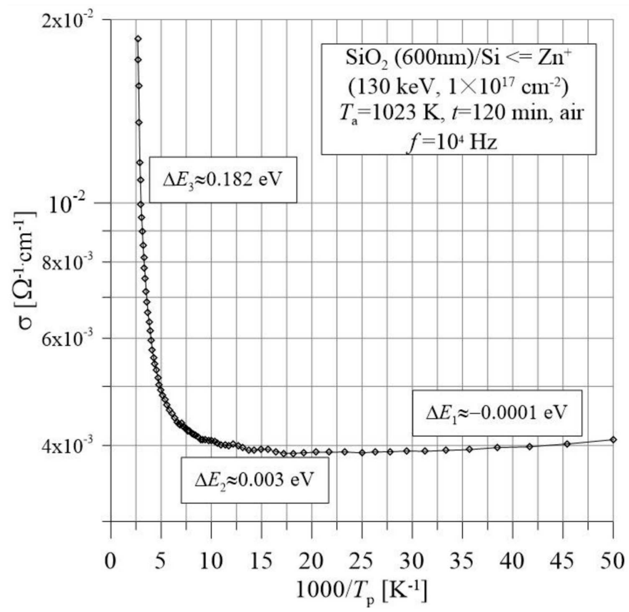

Fig. 3. Arrhenius dependence of conductivity σ at frequency $f = 10^4$ Hz of nanocomposite Zn–SiO_2 annealed at temperature $T_a = 750\,^{\circ}$C for $t = 120$ min.

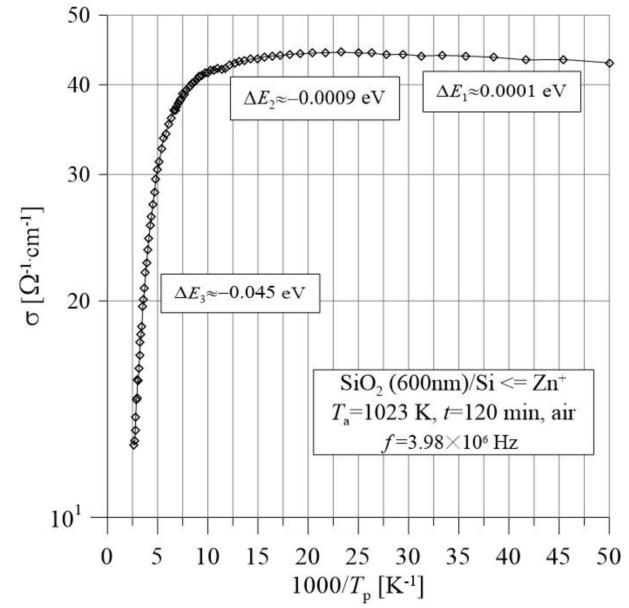

Fig. 4. Arrhenius dependence of conductivity σ at frequency $f = 3.98 \times 10^6$ Hz of nanocomposite Zn–SiO_2 annealed at temperature $T_a = 750\,^{\circ}$C for $t = 120$ min.

is marked with a minus sign. The temperature rise causes the material to exhibit the dielectric charge transfer mechanism. In the temperature range 60–180 K the activation energy is $\Delta\ E_2 \approx 0.003$ eV and at high temperatures 330–375 K it is much larger and amounts to $\Delta\ E_3 \approx 0.182$ eV. The situation is completely reversed in the high frequency range. At the low temperatures 20–45 K the activation energy is $\Delta\ E_1 \approx\ 0.000$ eV, and with a further increase in temperature in the range 45–120 K, $\Delta\ E_2\ \approx$ -0.0009 eV and for the interval 220–375 K, $\Delta\ E_3 \approx$-0.045 eV. This corresponds to the metallic type of conduction at higher temperatures. This metallic behaviour may be due to the appearance of a Zn impurity conduction band in the forbidden band of the SiO_2 dielectric which is thermally activated and occupied only under higher frequency conditions.

4. Conclusion

Based on the photoluminescence studies of Zn-SiO_2 thin films obtained by zinc ion implantation with energy 130 keV and fluence 1×10^{17} ion cm^{-2}, it was determined that the PL spectra of the as-implanted sample exhibit a blue-green band. This band is caused by the formation of oxygen vacancies in silicon dioxide. The increase of PL intensity via annealing can be explained by formation of ZnO phase. AC measurements show the hopping charge transfer mechanism between the Zn and ZnO nanoparticles in the range of lower measurement frequencies and metallic conduction through Zn impurities conduction band at high frequencies.

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