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Conduction and reversible memory phenomena in Au-nanoparticles-incorporated TeO_2–ZnO films

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ABSTRACT

A reversible memory behavior in TeO_2–ZnO thin films containing Au nanoparticles prepared using the sputtering technique has been observed. The current–voltage characteristics of the films, having Al and Si as electrodes, showed a switching behavior starting from an initial state of low conductivity to a high conductivity one. As a result, an abrupt increase of current (10^{-7} to 10^{-3} A) was observed for 6.5 V (100 nm thickness). Au nanoparticles provide a larger electron storage capability, and do not favor the transport through the insulator; they present a higher trapped charge concentration, which reduces the leakage current to lower levels. The influence of the Au nanoparticle diameter and volumetric concentration to reach the abrupt current transition and the value of the transition voltage was studied. These parameters were found to play an important role on reversible memory phenomena as they determine the facility/difficulty to fill and saturate the traps (Au nanoparticles) with electrons.

1. Introduction

TeO_2–ZnO thin film glasses exhibit physical properties that make them attractive candidates for semi-insulating materials: long-term chemical stability when compared to other types of glasses and control of the semi-insulating properties due to the binary phase when compared to silicate glasses [1]. These materials are intended for applications as waveguides [2] photovoltaic cells [3] passivating materials for power devices, such as thyristors and power transistors [4,5] and varieties of electronics [6,7].

Nowadays, much attention is paid to memory devices that utilize nanomaterials with bistable properties [8–10], such as Au nanoparticles that have been incorporated in polystyrene matrix to form a bistable memory device. Upon applied voltage, which exceeds a certain value, the conductivity changes abruptly from a state of low conductivity to another one of high conductivity with a difference of several orders of magnitude. This state of high conductivity will be memorized until a negative bias is applied to erase it [11].

Several models have been proposed to explain the bistable memory effect in nanomaterials. The proposed mechanisms have been based on the current transport through available energy levels, either by internal charge transfer between the donor–acceptor pairs or by the hopping process due to the charged or noncharged metallic nanomaterials [12]. Recently, the carrier transport path through metallic nanoparticles was investigated in organic matrices, especially the rapid increase on the current from the state of low conductivity to the state of high conductivity [11].

In this paper, the conduction and the reversible memory behavior in Au-nanoparticles-incorporated TeO_2–ZnO thin films is investigated. The influence of the Au nanoparticle diameter and volumetric concentration on the bistable characteristics are also discussed.

2. Material and methods

TeO_2–ZnO thin films with Au nanoparticles have been grown by RF magnetron co-sputtering method (14 MHz, model PV300 from Prest-Vacuo). Films were deposited on silicon wafers, with 7.6 cm diameter and a <100> crystallographic orientation with a resistivity ranging from 1 to 10 Ω cm. The cleaning of the silicon wafers was done by a conventional Radio-Corporation-of-America RCA standard clean [13] followed by a final dip in diluted hydrofluoric acid solution (d-HF) to remove the thin surface oxide.

For the production of the ceramic targets, the starting powders of TeO_2 and ZnO with purity of 99.999% were mixed and then submitted to 8 t uniaxial press, followed by sintering at 515 °C for 10 h. Targets with a 5 cm diameter and a 0.4 cm thickness were obtained with the following final stoichiometry: $(TeO_2)_{3.3}$–ZnO. Two targets were sputtered simultaneously for the production of the films with Au nanoparticles: the ceramic one (Target 1) presented above, and the gold one (commercial, Target 2), with a purity of 99.99%.

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Before the film deposition, the base pressure was of 6.7×10^{-3} Pa to minimize the presence of contaminants. Argon/oxygen plasma was used in the deposition process at 6.7×10^{-1} Pa (argon flux of 18 sccm and oxygen flux of 6 sccm). Target 1 was sputtered at 50 W RF power to prevent damage and Target 2 at 6 W RF. The substrate was maintained at a constant temperature during the deposition process (room temperature). Different deposition times were used and thin films with different thicknesses were then produced: 100 and 500 nm, using 75 and 360 min, for the deposition time respectively. The films were annealed at 325 °C, in air, for 10 and 20 h in order to see the influence on the Au nanoparticles diameter [14]. Finally, a thin film without annealing was produced. TeO_2–ZnO samples with Au nanoparticles produced, were: 100 nm—10 h, 100 nm—20 h, 500 nm—10 h, 500 nm—20 h, and 100 nm—without annealing. TeO_2–ZnO thin films with 100 nm thickness and without Au were also annealed during 10 and 20 h. Then, aluminum was evaporated (1 μm thick) through a mechanical mask to define the area of the Metal–Insulator–Semiconductor (MIS) structures ($A = 7.8 \times 10^{-3}$ cm^2). Fig. 1 presents the schematic diagram of the produced MIS capacitor.

Transmission electron microscope (TEM) was used to determine the size distribution of the nanoparticles and the crystalline nature of the obtained structures by means of electron diffraction analysis. The size distributions of the nanoparticles were determined by measuring each individual particle observed in the micrographs with the aid of the Image J, a public domain Java image processing program. Electron diffraction measurements were performed to determine the crystalline structure of the nanoparticles according to JCPDS-ICDD database [15]. For these measurements, the samples were milled, mixed with distilled water, and partially decanted. The floating part was taken by using a metallic screen and analyzed by TEM.

Rutherford Backscattering Spectrometry (RBS) spectra were taken at 2.2 MeV under normal incidence of a $4He^{+}$ beam and with a scattering angle of 170° using an accelerator Pelletron-Tandem, model 55 DH/NEC. The spectra were fitted with the aid of the SIMNRA 6.0 code [16] to obtain the Te, Zn, O and Au aerial concentrations.

After fabrication, MIS capacitors were electrically characterized with the aid of an Agilent 4156C Precision Semiconductor Parameter Analyzer (accuracy of 0.1%) to obtain parameters from the current–voltage (I–V) characteristics. Leakage current was measured submitting the capacitors to an external voltage ramp and then recording the I–V characteristics. The electrical measurements were performed at room temperature for all thin films.

3. Results and discussion

Fig. 2 shows typical results of electron diffraction and TEM measurements for TeO_2–ZnO thin films (100 nm thickness) with Au nanoparticles, without annealing (Fig. 2a) and annealed during 20 h (Fig. 2b). Table 1 shows the Au aerial concentration as well as the Au nanoparticles diameters for TeO_2–ZnO thin films, annealed during 10 and 20 h [17], and without annealing. It is worth of note that, in this last case, the Au nanoparticles appear stacked and with non-homogeneous distribution; so their contour had to be separated during image processing to consider the nanoparticles with spherical-type features. An average nanoparticles diameter increase of 159% is observed when the annealing time is increased from 10 h to 20 h, for 100 nm thickness. Also for annealing of 10 h, an average diameter increase of about 20% is observed when the thickness is increased from 100 nm to 500 nm. Electron diffraction measurements, presented as inset of Fig. 2(a) and (b), enabled the determination of the polycrystalline nature of Au nanoparticles; this was performed using the interplanar distances, extracted from the electron diffraction measurements (insets of Fig. 2a and b) and compared to the main intense peaks (0.236, 0.204, 0.144, 0.123 and 0.118 nm) of the Au diffraction pattern (not shown), according to the JCPDS-ICDD database [15]. Before annealing, peaks that correspond to both Au and AuO were observed, which appeared due to the use of argon/oxygen plasma [18] during the co-sputtering of Au/TeO_2–ZnO. AuO peaks decreased with the increase of the annealing time at 325 °C thus indicating that the amount of oxidized gold incorporated in the TeO_2–ZnO matrix decreased.

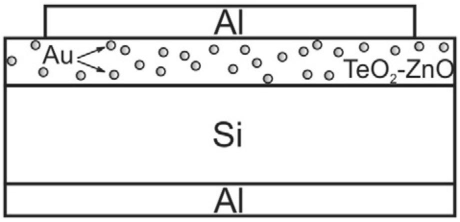

Fig. 1. Schematic diagram of produced MIS capacitor containing Au nanoparticles.

RBS results shown in Fig. 3 demonstrate the presence of the matrix elements (Te and Zn) and of Au, confirming the matrix stoichiometry of $(TeO_2)_{3.3}$–ZnO. The results presented in Table 1 show that the Au aerial concentration increases when the thickness (t) increases from 100 nm to 500 nm, for the same annealing time of 10 h. However, the Au aerial concentration (N_P) increases 4.5 times when the thickness increases 5.0 times, which means a lower volumetric concentration ($N_V = N_P / t$) for 500 nm thick films (approximately 10% lower) compared to the one with 100 nm thickness. Also, an increase of the nanoparticles diameter (d_P) of about 20% for 500 nm thickness (see Table 1) is observed. As a result, based on these two effects, we can conclude that the volumetric concentration of Au nanoparticles (N_{VP}) also decreases when the thickness increases from 100 nm to 500 nm, since N_{VP} is proportional to $N_V = N_P / t$ and decreases a little more when d_P increases. In addition, the volumetric concentration of Au nanoparticles, for the 100 nm thickness before annealing, decreases when compared with the one annealed during 10 h, since the Au nanoparticles diameter is more than the double and the Au aerial concentration is lower (see Table 1). As already mentioned before, a stacking effect was observed, for Au nanoparticles in the TeO_2–ZnO thin films (100 nm thickness), before annealing. This effect is correlated to the higher dispersion of the aerial concentration (see Table 1), which is also related to the nonuniform gold distribution along the sample area, possibly due to a nonuniform gold nucleation during the co-sputtering of Au/TeO_2–ZnO. Co-sputtering of Au/glass in argon/oxygen plasma, as performed in this work, enables the formation of partially oxidized gold species, which are incorporated in the glass matrix [18,19]. The results obtained from the diffraction pattern in Fig. 2a indicated the presence of a small amount of AuO along with Au. On the other hand, as reported by Vu [20], the partially oxidized state of gold in the layer must be favoring the Au nanoparticles disaggregation during the thermal annealing [21]. So, this disaggregation leads to a decrease of the average nanoparticle size; then a more uniform distribution takes places due to the Au dissolution in the layer as depicted by the lower standard deviation related to 10 h annealing, presented in Table 1 [20]. For 20 h annealing, the Au nanoparticle size increases, which means a predominant mechanism of coalescence [19] since the amount of oxidized gold possibly became negligible during the 20 h annealing. Also, it is important to call attention that the dissolution mechanism was predominant for 10 h because the amount of oxidized gold was possibly high enough to promote the dissolution [20]. As a result, Au nanoparticles with higher diameter and higher standard deviation are obtained for 20 h, as shown in Table 1.

Fig. 4a shows a typical I–V characteristics (logI × V) for TeO_2–ZnO thin films (100 nm thickness) with Au nanoparticles, without annealing. We observe a state of low conductivity (from 1×10^{-10} to 1×10^{-6} A) recorded from 0 to 40 V for the first voltage scan, which corresponds to "0" state of a bistable memory. The device was kept in the state of low conductivity until the applied voltage achieved 40 V. Then, an abrupt current transition from 1×10^{-6} to ~2×10^{-4} A was observed, while reducing the voltage again from 40 V, the current