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Structure and optical parameters of Eu doped tellurium oxide thin films prepared by reactive magnetron sputtering method

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Abstract

In this work the structural properties and photoluminescence of tellurium dioxide thin films doped by europium were described. Thin films were deposited by magnetron sputtering method and simultaneously heated at 200 °C. Presence of Eu ions and their valence states was confirmed by X-ray photoemission spectroscopy measurements. The structure of the films as well as the influence of europium dopant on crystalline structure of the films was examined by X-ray diffraction method. Morphology of the samples was observed by atomic force microscope. Doping by europium didn't change structural parameters. Optical measurements showed photoluminescence from Eu^{2+} and Eu^{3+} ions. However, in the spectrum there is no line corresponding to $^5D_0 \rightarrow {}^7F_2$ transition due to an electric-dipole transition, usually present in amorphous surrounding.

Keywords: Thin films; magnetron sputtering; tellurium oxides; europium dopant; photoluminescence

Introduction

Various techniques can be used to prepare tellurium dioxide thin films such as sol-gel method, thermal evaporation or magnetron sputtering [1-5]. Among these methods magnetron sputtering seems to be the most utilized way which can be optimized to obtain thin films with desired composition and properties [6-10]. Tellurium dioxide (TeO_2) is an important material due to its interesting physical and chemical properties [1, 2]. In particular, both crystalline and amorphous tellurium dioxide is one of the most suitable semiconductor materials [1, 2]. TeO_2 exhibits p-type of electrical conductivity with the energy gap equal 3.75 eV [11-13]. On the other hand, among variety of host matrices for optically active rare earth ions tellurium dioxide seems to be one of the most promising choices. Low phonon energies, high refractive index and high transparency in visible light range make them excellent candidates for matrix for rare earth dopants materials for luminescence applications [13-17]. Due its properties, TeO_2 can be used in a various practical applications in a field of optics, electronics and optoelectronics. High transparency in the IR region (better than in SiO_2 and GeO2 based materials) make it suitable for waveguides and optical fibers applications [1-3, 11, 18]. High Raman scattering makes tellurium dioxide suitable material for fiber amplifier. Amplifiers based on doped TeO_2 have a dozen times stronger higher gain than silica based elements [19]. Tellurium dioxide thin films could be manufactured by both, physical and chemical techniques. Such as magnetron sputtering, thermal evaporation, sol-gel, and chemical vapour deposition (CVD) methods [2, 11]. On the other hand, manufacturing of TeO_2 thin films doped with rare earth ions seems to be an innovation approach. In our previous works, we successfully synthesized tellurite-based glasses doped with rare earth ions. By changing the Europium and Dysprosium ions (Eu^{3+}/Dy^{3+}) ratio and by adjusting the excitation wavelengths we achieved simultaneous, color-tunable, long-lifetime luminescence [15, 17, 20]. In this work, we used reactive magnetron sputtering method for tellurium dioxide doped with Eu ions thin films deposition. In general, Ln^{3+} ions are characterized by an incompletely filled 4f shell. The 4f orbital is shielded from surroundings by filled $5s^2$ and $5p^6$ orbitals. This screening leads to relatively small influence of the host lattice on Ln^{3+} ions optical transitions. Although, some of the transitions in rare earth ions are hyper-sensitive to the crystal field of the matrix. An excellent example of this behavior are Eu^{3+} ions, with hyper-sensitive line corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition. This is very important and can affect the color of the emitted light. On the other hand, the emission of Eu ions can also give some hint as to the matrix in which they are dispersed.

In this work, we studied structural and luminescence properties of Eu doped thin TeO_2 films. Our results confirmed that amorphous tellurium dioxide thin films are suitable matrix for optically active rare earth ions.

Experimental

All, metallic and oxides thin films were prepared by radio frequency reactive magnetron sputtering technique. Metallic Te target and Te-Eu mosaic target with diameter of 50.8 mm were sputtered for about 45 min in argon-oxygen atmosphere what resulted in 300 nm film thickness deposition. The pressure in the chamber was below 0.2 Pa and substrate was heated at 200 ^{o}C. The distance between sputtered targets and the Corning 1737 glass substrate was about 10 cm. Films deposition parameters are presented in Table. 1.

Chemical composition of prepared samples was analyzed by X-ray photoemission spectroscopy method (XPS). The XPS measurement was performed at room temperature under ultra-high vacuum conditions, at pressures below 1.1×10^{-6} Pa by Omicron NanoScience equipment. Data analysis was performed with the CASA XPS software package using a Shirley background subtraction and least-square Gaussian-Lorentzian – GL(30) curve fitting algorithm. The spectra obtained were calibrated to give a binding energy of 285.00 eV for C 1s. Crystal phase was determined by X-ray diffraction (XRD) method. Philips X'Pert diffractometer system with a Cu-filtered Kα radiation in a range of 10^{o} – 80^{o} of 2θ was used for XRD measurements. The NT-MDT Ntegra Aura atomic force microscope (AFM) was used for imaging of the surface morphology. AFM images were recorded in the contact mode. Optical transmission characteristics were recorded with Evolution 220 UV-Visible Spectrophotometer in a range of 250 nm - 1100 nm. The effect of Eu-dopant on luminescence of prepared films was examined by photoluminescence spectroscopy (PL). Luminescence emission spectra were collected by Horiba Jobin Yvon spectrofluorometer (Fluorolog 3) using an excitation wavelength of 395 nm. All measurements were conducted at room temperature.

Results

In order to find optimal manufacturing parameters, like plasma composition, to obtain pure TeO_2 thin films the influence of the Ar/O_2 ratio during deposition process on the chemical composition of the films was examined. First of all, it can be seen that deposition ratio is higher for metallic films prepared in pure argon plasma. The lower deposition rate during process in mixed argon-oxygen and pure oxygen plasma could be considered due to the reduction in the sputtering yield resulting from the mass difference between Ar and O_2 [21]. The effect of sputtering gas composition on the tin films chemical composition was investigated by XPS measurement. Fig. 1 shows the XPS spectra of the selected tellurium based samples. One can ~~be~~ see relation between working gas composition and chemical composition of deposited films. Increasing of oxygen content resulted in increasing peaks at 576.1 eV and 586.4 eV what indicates on increasing of tellurium dioxide phase. On the basis of XPS results the Te^{4+}/Te^{0} ratio was calculated for samples prepared under various Ar/O_2 composition. The nearly linear dependence of the Te^{4+}/Te^{0} ratio is presented on Fig. 2. It is clearly evident that only the sample produced under pure oxygen plasma consist only tellurium dioxide phase.

XRD results of prepared thin films are presented in Fig. 3. XRD patterns show tellurium crystalline phase for samples with leak of tellurium oxide phase (Fig. 3, curve a and b) while for the films with high content of tellurium dioxide no crystalline phase was observed (Fig. 3, curve c). A broad bulge between the 2θ angle 15^{o} and 35^{o} arises from the corning glass substrate. However, by comparing the presented diffractograms (going from the curve a to d) one can notice that the size of mentioned above broad bugle is changing. This kind of broad bump is typical of amorphous materials and arises from the short-range order in material. The observed increase in its size may indicate a higher content of the amorphous phase in the sample. On the other hand, it should be noted, that a very small amount of crystalline phase could not be noticed in the XRD study, especially when it consists of nanocrystals. On the basis of the results of XPS and XRD measurements of prepared samples an amorphous film prepared under pure oxygen plasma was chosen as a matrix for TeO_2:Eu films. The XRD pattern of TeO_2:Eu film is presented on curve d in Fig 3. It is clearly visible that doping of tellurium dioxide by Europium has no influence on crystal structure.

Presence of Eu dopant was confirmed by XPS method (Fig. 4). Recorded spectrum was deconvoluted into four peaks at 129.4 eV and 135.0 eV, with the energy separation of 5.6 eV corresponding to Eu^{2+}, while peaks at 135.9 and 141.6 eV with energy the separation of 5.7 eV correspond to Eu^{3+} [22, 23]. On the basis peaks' area relative contribution of Eu^{2+} and Eu^{3+} was calculated to be 21% : 79%.

The effect of Eu dopant on the surface morphology of TeO_2 thin films was examined by AFM (Fig. 5). As it can be seen, the surface of TiO_2:Eu sample is homogeneous without any cracks. It consists of grains in size of ca. 60 nm. Presence of europium ions caused increase of the grain size up to ca 120 nm - 130 nm.

The light transmission spectra for manufactured undoped and doped thin films are presented in Fig. 6. It is observed that both samples are well transparent in a visible range, with transmission coefficient is equal ca. 70% at 550 nm The absorption edge did not shift significantly after Eu doping and is equal 278 nm and 282 for undoped and doped sample, respectively. In the spectrum of thin film doped with Eu^{3+} ions two characteristic peaks at 466 nm and 526 nm can be observed. This absorption bands are characteristic to transitions from the ground state $^7F_0$ to the $^5D_2$ and $^5D_1$ excited states [17, 24]. On the basis of transmission spectra, the Urbach energy (E_U)was calculated and Tauc plots for direct allowed and indirect allowed transitions were prepared (Fig. 7). The value of Urbach energy is often interpreted as the width of the tail of localized states and is also used to quantity the degree of structural disorder [25, 26]. Larger value of E_U for TeO_2:Eu film can be attributed to increase of structural disorder [27]. The values of the optical band gap width for prepared samples were obtained from approximation of linear parts of Tauc plots [27]. It is clearly visible that optical band gap of tellurium dioxide decrease after doping by europium ions. Optical parameters are collected in Tab. 2.

Fig. 8 shows emission spectrum of TeO_2:Eu monitored with an excitation wavelength of 395 nm. In 450 – 650 nm spectral range three low intensity peaks may be distinguished. All of them correspond to Eu^{3+} relaxation from excited states: $^5D_2 \rightarrow {}^7F_3$ (506 nm), $^5D_1 \rightarrow {}^7F_2$ (553 nm) and $^5D_0 \rightarrow {}^7F_1$ (587 nm). Low intensity is probably caused by the small thickness of the layer and additionally a small content of Eu^{3+} ions in it. Unfortunately, the bands characteristic for Eu^{2+} ions are not visible in the spectrum, which of course may be due to the small content of these ions in the sample. But on the other hand, the emission spectrum of Eu^{2+} ions dispersed in a solid state matrix has a broad band character. It is because the emission is interconfigurational, i.e. $4f^65d \rightarrow 4f^7$ [29, 30]. The position of this broad peak strongly depends on the crystal field of the Eu^{2+} surroundings. When Eu^{2+} ions occupy different crystallographic sites in a host lattice, then more than one emission band can be observed. In the case of the samples studied in this work, the matrix is amorphous, i.e. in the range of the wavelength tested here, only one emission band with a maximum around 500 nm would be observed [31]. This band may overlap slightly with the peak of Eu^{3+} with a maximum at 506 nm. It is therefore difficult to distinguish whether the band at 506 nm corresponds to Eu^{2+} or Eu^{3+} ions. The peaks observed in the spectrum seem to be broad, which usually happens in a situation where Eu^{3+} ions are distributed in the amorphous matrix. The screening of 4f orbital, originating from the surrounding 5s and 5p orbitals, which are completely filled, leads to relatively small influence of the host lattice on Eu^{3+} ions optical transitions. The bands do not change their positions, but some of them are hyper-sensitive to the local symmetry. What's interesting, in the spectrum presented in Fig. 8 there is no line corresponding to $^5D_0 \rightarrow {}^7F_2$ (614 nm) transition, usually present in amorphous surrounding, or in crystals with a deviation from inversion symmetry [32, 33]. This is the band hypersensitive to the local symmetry and due to an electric-dipole transition. In TeO_2 based glass containing Eu^{3+} ions this band was observed as one of the most intense emission bands [17, 34]. Similarly, this band was most intense in crystalline α-Te_2:Eu^{3+} nanoparticles, manufactured by the hydrothermal method [35] In present work the most intense peak, observed at 587 nm, is caused by a magnetic- dipole transition, which is not sensitive to the crystal field. This situation is predominant in the systems in which Eu^{3+} ions occupy lattice position with inversion symmetry. Presented here TeO_2 films are amorphous and most probable formed by the unit structure typical for glasses [36], so the lack of $^5D_0 \rightarrow {}^7F_2$ (614 nm) transition is not in this moment clear and needs future experiments.

Summary

In present work the structure and emission spectra of thin TeO_2 films doped with Eu ions were studied. The structure of the films depends on preparation atmosphere. It was concluded from XPS results, that films were metallic after preparation in pure argon plasma and built from tellurium dioxide, when pure oxygen plasma was used during experiment. This result was confirmed in XRD experiments. The XRD results also showed that the layers are amorphous. It was observed that the TeO_2 samples are well transparent in a visible range, with transmission coefficient equal ca. 70% at 550 nm, so they could be used as a matrix for Eu ions. Larger value of Urbach energy of Eu ions doped samples, calculated on the basis of transmission characteristic, indicate the increase of structural disorder in the films in comparison with pure TeO_2 films. The emission spectrum consists of peaks corresponding to Eu^{3+} relaxation from excited states. In the spectrum there is no line at 614 nm, usually present in amorphous surrounding and hypersensitive to the local symmetry, what is not in this moment clear and needs future experiments. However, on the basis of the results presented in this paper, it can be concluded that amorphous thin layers of TeO_2 can be promising matrix for optically active rare earth ions.

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