Preparation and Characterization of Tin Tungstate Thin Films

A. KUZMIN, * M. ZUBKINS, AND R. KALENDAREV

Institute of Solid State Physics, University of Latvia, Kengaraga Street 8, LV-1063 Riga, Latvia

Tin tungstate thin films were prepared by dc magnetron sputtering method and studied by x-ray diffraction, confocal microscopy and Raman spectroscopy. It is shown that the films are composed mainly of nanocrystalline $\alpha$-SnWO$_4$ phase. The possibility to use these films as write-once optical recording media is demonstrated.

Keywords Tin tungstate; thin film

1. Introduction

Tungstates have received considerable attention from both theoretical and technological point of view already for a century. Their wide range of chemical and physical properties is determined by a type of metal cation and tungsten oxyanion. In particular, noncentrosymmetric tungstates represent considerable interest due to piezoelectric, ferroelectric and nonlinear optical properties [1, 2]. Many wide band-gap tungstates are promising materials for scintillators [3, 4], solid state laser hosts [5] and Raman shifters [5–7]. The optical properties of tungstates can be controlled by composition [8] and crystallites size-reduction down to nanoscale [9]. The electrical properties of narrow band-gap tungstates found applications in semiconducting oxide gas sensors [10]. Thin film tungstates have been studied for the use as electrochromic materials [11], for phase-change optical recording [12], as electrodes in batteries [13] and photoanodes for water oxidation [14].

Among large family of tungstates, tin tungstate (SnWO$_4$) has been much less studied. It crystallizes at low-temperatures (below 670°C) in $\alpha$-SnWO$_4$ phase, having orthorhombic crystal structure and dark-red color [15]. Tin tungstate is a promising gas-sensing and photocatalytic material [16–18], also suggested for the use as an anode material in Li-ion batteries [19]. Besides, thin films of tin tungstate are of significant interest because of their possible use in transparent electronics. A possibility to produce tin tungstate thin films having both p-type or n-type electrical conductivity has been proposed recently in [20].

The specific properties of $\alpha$-SnWO$_4$ are determined by its crystal structure, which is composed of 2D sheets of distorted WO$_6$ octahedra, separated by layers of Sn$^{2+}$ ions, also coordinated by six oxygens [15]. The WO$_6$ octahedra within a sheet are joined by...
four corners, and their distortion is related to an off-center displacement of $W^{6+}$ ions due to the second-order Jahn-Teller effect (SOJT) [21]. The pair of stereochemically active Sn 5s electrons is responsible for “lone pair” distortion of SnO$_6$ octahedra via the SOJT effect [22].

The optical and electrical properties of $\alpha$-SnWO$_4$ are determined by its electronic structure. The band gap of $\alpha$-SnWO$_4$ phase is indirect and equal to 1.64 eV [22]. The results of the first principles calculations [22, 23] suggest that the valence band in $\alpha$-SnWO$_4$ is mainly composed of strongly interacting O 2p and Sn 5s states, whereas the conduction band has W 5d-O 2p antibonding character with an admixture of Sn 5p states. It was shown in [20] that by changing the composition (Sn:W:O ratio) the Fermi level can be pushed into the valence or conduction band, thus allowing one to control the type of conductivity.

In this study we report on the preparation of tin tungstate thin films by dc magnetron sputtering method and on the characterization of the films morphology and phase composition using several techniques as x-ray diffraction, confocal microscopy and Raman spectroscopy.

2. Experimental

Tin tungstate thin films were produced from metallic tungsten (99.95%, Heraeus) and tin (99.99%, Heraeus) targets by reactive magnetron sputtering in a plasma-focusing dc magnetic field. First, the multi-layer structures WO$_{3-y}$/SnO$_x$/glass were deposited using consecutive sputtering processes: such films will be referred as “as-prepared”. During the deposition the glass substrate was kept at room temperature, and the sputtering was conducted at 0.5 Pa working pressure and 100 W sputtering power. Deposition time for SnO$_x$ and WO$_{3-y}$ layers was 5 and 10 minutes, respectively. The total film thickness, measured by profilometer Veeco Dektak 150, was about 500 nm. A gas mixture of argon and oxygen was used as the sputter atmosphere. Three different thin films (TF1, TF2, TF3) were produced by changing the Ar:O$_2$ ratio during tin oxide layer deposition to have the layer composition close to SnO: Ar:O$_2$ = 10:3 for TF1, Ar:O$_2$ = 10:2.5 for TF2 and Ar:O$_2$ = 10:2 for TF3. The ratio Ar:O$_2$ = 10:6 was used during tungsten oxide layer deposition. Next, the thin films were annealed at 450°C in a vacuum. Upon annealing, a reaction of tungsten and tin oxides leads to a formation of nanocrystalline tin tungstate film. Note that annealing in air results in the formation of two-phase film composed of crystalline WO$_3$ and SnO$_2$.

The phase composition of thin films was studied by x-ray diffraction using Bruker D2 PHASER $\theta$-$\theta$ diffractometer equipped with copper anode x-ray tube.

Confocal spectromicroscopy and Raman scattering spectroscopy were performed using a confocal microscope with spectrometer Nanofinder-S (SOLAR TII, Ltd.). All experiments were conducted in back-scattering geometry at room temperature (20°C) through Nikon CF Plan Apo 100× (NA=0.95) optical objective. Diode-pumped solid-state (DPSS) Nd:YAG laser (532 nm, max cw power $P_{ex}$ = 150 mW) was used as the excitation source, and the spectra were dispersed by 600 grooves/mm diffraction grating mounted in the 520 mm focal length monochromator. The elastic laser light component was eliminated by the edge filter (Semrock LP03-532RE). Peltier-cooled back-thinned CCD camera (ProScan HS-101H) was used as a detector in Raman scattering experiments, whereas the Hamamatsu R928 photomultiplier tube was employed in confocal-spectral imaging experiments. To avoid possible sample damage, the laser power at the sample was controlled by a variable neutral-density filter (OD = 0–3) during imaging.
Finally, the central part of the films, subjected to annealing at 450°C in a vacuum, was intentionally exposed to 532 nm laser radiation $P_{ex} = 10 \text{ mW/μm}^2$ to test possibility of its use for optical recording.

3. Results and Discussion

X-ray diffraction patterns of annealed thin films TF1, TF2 and TF3 (Fig. 1) indicate that they are nanocrystalline and are mainly composed of $\alpha$-SnWO$_4$ phase [25], with some admixture of SnO [24] and $\beta$-SnWO$_4$ [26] phases, as well as very small amount of Sn$_{0.25}$WO$_3$ [27] phase.

Raman scattering spectra of the thin films are shown in Fig. 2. The two bands at 115 cm$^{-1}$ and 210 cm$^{-1}$ in the as-prepared films are attributed to B$_{1g}$ and A$_{1g}$ modes of SnO [28], whereas the two remaining broad bands at $\sim$750 and $\sim$950 cm$^{-1}$ are, respectively, due to the stretching modes of the bridging oxygens O-W-O and of the terminal W=O bonds in amorphous a-WO$_3$ [29]. After annealing at 450°C in a vacuum, tin and tungsten oxides react to form $\alpha$-SnWO$_4$, characterized by the main Raman band at 780 cm$^{-1}$ and the small band at $\sim$280 cm$^{-1}$ [25]. The origin of the main band at 780 cm$^{-1}$ is due to the stretching O-W-O vibrations within the distorted WO$_6$ octahedra. Note that close Raman spectra were observed previously for nanocrystalline $\alpha$-SnWO$_4$ produced by hydrothermal reaction method [19]. The broad peak at $\sim$920 cm$^{-1}$ in TF1 and TF3 can be tentatively attributed to some remaining contribution of amorphous a-WO$_3$ [12].

The homogeneity of the thin films and their sensitivity to laser irradiation were studied by confocal spectromicroscopy (Fig. 3). Confocal images show spotted morphology of the films annealed at 450°C in a vacuum (border part in Fig. 3(a)) and exposed to laser radiation (Fig. 3(c) and central part in Fig. 3(a)). Spectral images (Fig. 3(b,d)) were acquired at 780 cm$^{-1}$, therefore bright points correspond to the largest intensity of the main band in the Raman scattering spectrum of $\alpha$-SnWO$_4$ (Fig. 2(right panel)). A comparison of confocal and spectral images suggests that the dark regions in Fig. 3(a,c)
Figure 2. Raman scattering spectra of as-prepared (left panel) and annealed at 450°C in a vacuum (right panel) tin tungstate thin films.

Figure 3. Confocal (a,c) and spectral (b,d) images of TF2 thin film annealed at 450°C in a vacuum. Spectral images were acquired at 780 cm⁻¹. Image size: 32 μm × 29 μm (a, b) and 8 μm × 10 μm (c,d). Central part (c,d) of the film (a,b) was exposed to 532 nm laser radiation ~10 mW/μm².
correspond to the parts of Fig. 3(b,d) with the largest density of bright points and, thus, are composed mainly of nanocrystalline $\alpha$-SnWO$_4$. The laser treatment significantly modifies the optical contrast (reflectivity) of the films without modification of their phase composition. In fact, the crystallinity of the films is improved after laser irradiation as is evidenced by the stronger Raman signal from the main band at 780 cm$^{-1}$. Therefore, the use of tin tungstate thin films as write-once optical recording media is feasible.

4. Conclusions

The possibility to produce tin tungstate thin films composed mainly of $\alpha$-SnWO$_4$ phase by dc magnetron sputtering method was demonstrated. We employed novel layerwise deposition process followed by film annealing at 450$^\circ$C in a vacuum. The possibility to use these films as optical recording media is also shown.

Funding

This work was supported by European Social Fund project No. 2013/0015/1DP/1.1.1.2.0/13/APIA/VIAA/010.

References

10. V. Dusastre and D. E. Williams, Selectivity and composition dependence of response of wolframite-based gas sensitive resistors (MWO$_4$)$_x$([Sn-Ti]O$_2$)$_{1-x}$ (0<x<1; M=Mn, Fe, Co, Ni, Cu, Zn). *J. Mater. Chem*. 9, 965–971 (1999).


