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Confocal spectromicroscopy of amorphous and nanocrystalline tungsten oxide films

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Abstract

A Raman confocal spectromicroscopic system was used to study in situ phase composition and surface morphology in amorphous and nanocrystalline tungsten oxide and tungstate thin films, prepared on silicon and glass substrates by dc magnetron co-sputtering technique. The possible use of these films for the phase-change optical recording was demonstrated using 442 nm He–Cd laser with a variable power of up to 50 mW. The formation of nanocrystalline tungsten trioxide or tungstate phases was observed under the laser irradiation. These nanocrystalline phases show relatively strong Raman activity, which can be used for information reading purposes. A multilayer structure composed of several tungstate films with different chemical composition is proposed as potential write-once optical recording media.

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1. Introduction

Recent advances in optical recording technology are strongly related to an invention of blue-wavelength diode lasers and a development of compatible storage media [1]. Today an optical recording capacity of more than 25 GB per recording layer is achieved in 'Blu-ray' disks by using a laser with the wavelength of 405 nm, focussed through a high numerical aperture objective lens to a spot size of about 300 nm [2,3]. Such systems operate using the phase-change recording technology, i.e. laser-induced amorphous-to-crystalline phase transition in inorganic alloy films. The amorphous and crystalline phases have a different refractive index, that allows information readout using amplitude and/or phase modulation of the reflected laser. When a transition between the crystalline and amorphous phase is reversible, an information can be erased and/or overwritten many times.

The most frequently used rewritable phase-change recording materials, ternary GeSbTe and quaternary AgInSbTe alloys, belong to the group of semiconductor chalcogenides [1,4,5]. However, other compounds are subject of continuous investigation for optical recording media [4]. In particular, tungsten oxide, well known for its electrochromic properties [6], was studied in [7–11]. The use of a reversible photoredox reaction under two-wavelength laser excitation of tungsten oxide in air was proposed for optical memory media in [7,8]. The reflectance change upon heat treatment of WO_3/metal thin-film bilayered structures was studied in [9]. Rewritable electrically selective multilayered optical recording disk, based on the electrochromic behavior of WO_3, was suggested in [10]. Finally, the possibility for write-once optical recording was demonstrated in WO_2 film, fabricated by the pulsed laser deposition [11].

In this work, we report on the Raman confocal spectromicroscopy study of amorphous and nanocrystalline

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tungsten oxide and tungstate thin films for the use as phase-change write-once optical recording media.

2. Experimental

Pure tungsten oxide WO_3 and tungstate $NiWO_4$ and $ZnWO_4$ thin films (t.f.) were produced from metallic tungsten (99.95%), nickel (99.0%) and zinc (99.9%) targets by reactive magnetron co-sputtering in a plasma-focusing dc magnetic field [12,13]. A gas mixture of argon (80%) and oxygen (20%) was used as the sputter atmosphere. The sputter deposition was performed on silicon and glass substrates at a total gas pressure in the chamber about 6.7 Pa and a discharge power 100 W. The thickness of the films was about 300–500 nm. All 'as-deposited' thin films were X-ray amorphous.

All spectromicroscopic experiments were performed at room temperature using a 3D scanning confocal microscope with spectrometer 'Nanofinder-S' (SOLAR TII, Ltd.) [14]. The 'Nanofinder-S' system consists of an inverted Nikon ECLIPSE TE2000-S optical microscope connected simultaneously to a laser confocal microscope unit with high-sensitivity Hamamatsu R928 photomultiplier tube (PMT) and to a monochromator-spectrograph (SOLAR TII, Ltd., Model MS5004i) with attached Hamamatsu R928 PMT detector and Peltier-cooled back-thinned CCD camera (ProScan HS-101H, 1024×58 pixels). The color video CCD camera (Kappa DX20H) is used for optical image detection through the microscope. The image scanning is performed in the X–Y directions by galvanometer mirror scanners and in the Z direction by a piezo-scanner. A He–Cd laser (441.6 nm, 50 mW cw power) is used for scanning and spectroscopic measurements. All confocal images were obtained using the laser power about 15 mW and a pinhole of about 50 μm, whereas the higher laser power (25 mW or 50 mW) was used for recording. The measurements were performed through Nikon Plan Fluor $40 \times$ (NA = 0.75) optical objective. The Raman spectra were recorded using 600 grooves/mm diffraction grating with a resolution of about 3–4 cm^{-1} using the monochromator with 520 mm focal length and the edge filter to eliminate the elastic component.

3. Results and discussion

The confocal image and the corresponding Raman spectrum of the 'as-deposited' tungsten oxide thin film are shown in Fig. 1(a) and Fig. 2(b), respectively. The Raman signal consists of two weak bands, being typical for the amorphous tungsten trioxide (a-WO_3), whose structure is mostly composed of distorted [WO_6] octahedral groups joined by corners [12]. The broad band at 750 cm^{-1} is due to the stretching modes O–W–O of the bridging oxygens, and the band at 950 $cm^{-1}$is due to the stretching mode of the terminal W=O bonds [15]. Note that the last band is strongly overlapped with the second order Raman scattering from silicon substrate.

By using the 25 mW laser power, the rectangular image was recorded on a-WO_3 film and was clearly observed after that in confocal mode (Fig. 1(b)). At the same time, the corresponding Raman signal remained nearly unchanged (Fig. 2(c)), indicating that only few atomic layers close to the film surface were modified during writing process. Our experiments show that thus recorded image is unstable for a long time exposition of the film in air even at room temperature and can be completely bleached during the time from several minutes to several days. Similar effect has been observed by us previously in freshly ground polycrystalline WO_3 powders [16], where it was associated with a formation of metastable surface color centers, attributed to the reduced tungsten ions.

An increase of the laser power to 50 mW results in a-WO_3 thin film local crystallization, occurring normally above 400 °C. The crystalline regions show good contrast in confocal image (Fig. 1(c)) and exhibit the Raman signal with two strong bands at 712 cm^{-1} and 806 cm^{-1} (Fig. 2(d)), being due to the stretching modes O–W–O of the bridging oxygens [15]. However, some broadening of the bands and the ratio between two bands indicate [16] that crystallites have a size about one-two hundred nanometres.

The divalent transition metal tungstates AWO_4 with wolframite-type structure are members of a large family of structurally related compounds with the A^{2+} ion being Mg, Mn, Fe, Co, Ni, Cu or Zn. The wolframite structure consists of a hexagonal close-packed oxygen array in which

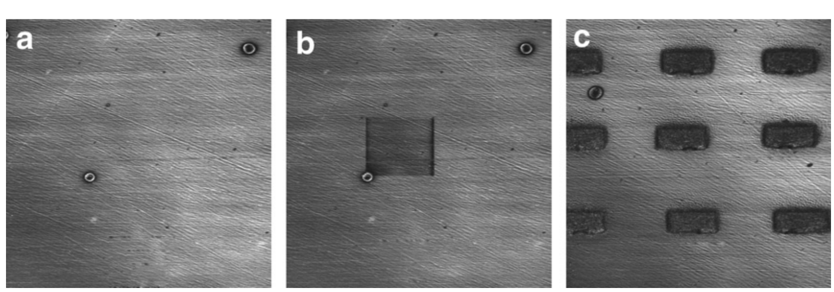

Fig. 1. Confocal images (274 μm × 333 μm) of (a) 'as-deposited' a-WO_3 thin film (b) after recording with 25 mW laser power and (c) after recording with 50 mW laser power.