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Phase modification and surface plasmon resonance of Au/WO_3 system

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ABSTRACT

We report the action of gold as catalyst for the modification of phase from triclinic WO_3 to monoclinic $W_{18}O_{49}$ and nucleation centre for the formation of $W_{18}O_{49}$ phase, in gold incorporated tungsten oxide films prepared by RF magnetron sputtering technique. A new band is observed near 925 cm^{-1} in the Raman spectra of gold incorporated tungsten oxide films which is not observed in the pure tungsten oxide film. The intensity of this band enhances with gold content. A localized surface plasmon resonance (LSPR) band is observed near the wavelength 604 nm in gold incorporated tungsten oxide films. The integrated intensities of LSPR band and Raman band ($\sim$925 cm^{-1}) can be used for sensing the quantity of gold in the Au/WO_3 matrix.

1. Introduction

Recently metal nanoparticles are getting great attention since they can be used as seed and nucleation centres for the preparation of nanoparticles of different materials [1] and can act as catalyst for the formation of various nanostructures [2–4]. Wu and Yang [2] have reported that the gold nanoclusters act as catalysts for the selective growth of Si nanowires with different diameters. Hanrathe and Korgel [3] have reported the fabrication of Ge nanowires of several micron length using alkanethiol-protected gold nanocrystals in seed wire formation. In our previous study [4], it is found that silver can act as a catalyst for the formation of nanocrystalline $W_{18}O_{49}$ phase in Ag/tungsten oxide matrix. Noble metal nanoparticles are also getting significant attention since they exhibit large optical nonlinearities and surface plasmon resonance in addition to their catalytic activity [5,6]. The localized surface plasmons (LSP) are quantized collective oscillations of conduction electrons against the positive ionic background in the presence of electromagnetic wave that can enhance and focus incident light to sub-wavelength dimension below the diffraction limit [7]. Surface plasmon resonance (SPR) technique is getting great attraction in sensor technology since it can be used for the detection of various physical, chemical and biological parameters [8–11]. The resonance frequency of the LSP band depends on the size and shape of nanoparticles, the nature of substrate and dielectric functions of surrounding medium and the particle spacing [5,12,13]. By tuning these parameters, the resonance frequency can be matched to any desired wavelength from visible to near-infrared region [14,15]. Since the localized surface plasmon resonance (LSPR) wavelength depends on size and shape of nanostructures and dielectric environment, by detecting the LSPR peak shift with refractive index/dielectric constant of surrounding medium, metal nanoparticles can be used as plasmonic sensors [12–19]. Controlling the arrangement of metallic nanoparticles and tuning their optical response are of significant importance for research of the intrinsic optical properties of nanoparticle structures [16] and for the expansion of related applications, such as surface enhanced Raman spectroscopy (SERS).

In the case of dielectric films deposited over gold coated substrates, the gold nanoparticles on the top surface can only be in contact with the dielectric particles. Hence, the overall distribution of nanoparticles throughout the dielectric matrix cannot be ascertained. Therefore, in this study we have dispersed different concentrations of gold nanoparticles in tungsten oxide powder and the mixture was used as target for RF magnetron sputtering. This paper reports the effect of gold incorporation in the phase modification of tungsten oxide and the surface plasmon resonance of gold nanoparticles in tungsten oxide matrix.

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2. Experimental methods

The gold incorporated tungsten oxide thin films were prepared by RF magnetron sputtering and controlled subsequent annealing. The target for sputtering was prepared from commercially available tungsten oxide powder (Aldrich, 99.995% purity) and gold powder (Aldrich, 99.99% purity). To the tungsten oxide powder, gold powder of desired proportions (0, 1, 2, 5 & 10 wt%) were mixed and the mixtures were dry ground for a duration of 3 h and the pressed mixtures were used as targets for sputtering. The sputter chamber was initially evacuated to a base pressure of 5.0×10^{-6} mbar using a rotary pump and a diffusion pump. Pure argon gas was admitted into the chamber and the argon flow was maintained at a pressure of 0.015 mbar. The target was powered through a magnetron power supply (Advanced Energy, MDX 500) operated at a power of 150 W. The films were deposited on quartz substrate kept at a distance 5 cm from the target and the deposition was done for duration of 30 min for all the films. The films, thus obtained, were annealed at a temperature of 600 °C in a controlled programmable furnace for duration of 1 h with a heating rate of 3 °C/min. The as-deposited films with gold incorporation concentrations 0, 1, 2, 5 & 10 wt% are designated as G0W0, G1W0, G2W0, G5W0 and G10W0 respectively and their annealed counter parts are designated as G0W600, G1W600, G2W600, G5W600 and G10W600 respectively.

The micro-Raman spectra of the samples were recorded using Labram-HR 800 (Horiba Jobin Yvon) spectrometer with a spectral resolution of about 1 cm^{-1} equipped with Peltier cooled Synapse CCD detector system. The spectra were recorded using an excitation radiation of wavelength 784 nm from a diode laser. The crystalline structure and crystallographic orientations of the films were characterized by X-ray diffraction (Philips, XPERT-PRO Diffractometer) measurements employing Cu $K\alpha_1$ radiation with a wavelength of 1.5406 Å in the 2θ range 10–70° with a step size of 0.001° in Bragg-Brentano geometry. The surface morphology of the films was characterized by employing (a) an atomic force microscope (AFM) in peak force tapping mode with a scan rate 1 Hz using silicon tip on silicon nitride lever having a force constant of 0.4 N/m (Bruker Model: Dimension Edge with Scan Asyst having Nano Drive software) and (b) a field emission scanning electron microscope (Nova Nano SEM-450 Model number 1027647, FEI, USA) equipped with an X flash detector (6/10 Bruker). The elemental analysis of the films was done using an electron energy dispersive X-ray spectrometer (EDS-Quantax 200, Germany) attached to the field emission scanning electron microscope (FESEM). The transmission and absorption spectra of the samples were studied using JASCO V-550 UV–vis double beam spectrophotometer. The thickness of the films was measured using Stylus profiler and lateral SEM image analysis.

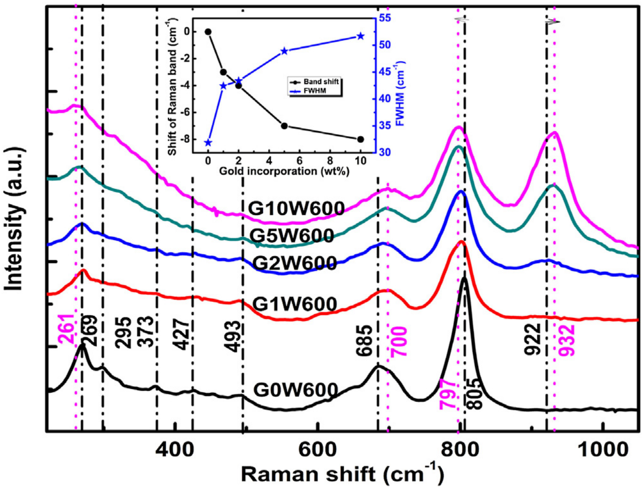

Fig. 1. Micro-Raman spectra of pure and gold incorporated tungsten oxide thin films annealed at 600 °C prepared by RF magnetron sputtering technique (excitation wavelength used is 784 nm). The figure in the insight represents the variation of FWHM and shift of band position of symmetric stretching band at 805 cm^{-1} with gold incorporation.

3. Results and discussion

3.1. Phase modification studies

Raman spectroscopy is a powerful non-destructive tool for elucidating the structural information of a material system. In metal oxide nanocomposites, the existence of new bands in the Raman spectra corresponds to the appearance of additional phase in base oxide, the change in the shape of Raman spectra indicates the change of chemical or crystallographic structure, the spreading of Raman bands corresponds to a change of grain size and strain in the films and the shift of Raman band position represents the change of lattice constants [20–26]. Therefore, to identify the structural changes and formation of new phase, if any, micro-Raman spectral analysis of the samples are recorded using an excitation wavelength of 784 nm. The micro-Raman spectra of pure and gold incorporated tungsten oxide films annealed at a temperature of 600 °C are shown in Fig. 1. Micro-Raman spectrum recorded for WO_3 bulk (powder) is shown in Fig. 2a and that of $W_{18}O_{49}$ phase is shown in Fig. 2b. The Raman spectrum of the WO_3 bulk sample presents five prominent intense bands along with a few bands of less intensity. The most intense Raman band at 804 cm^{-1} and the intense band at 714 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibrations of W^{6+}—O bond corresponding to the WO_3 phase [27]. The Raman bands in the wavenumber region 200 – 450 cm^{-1} can be due to the bending vibrations of O—W—O bond and the bands obtained below 200 cm^{-1} can be due to lattice vibration modes. The Raman spectrum of the pure WO_3 film (G0W600) presents a very intense band at 805 cm^{-1} and an intense band at 687 cm^{-1} obviously due to the symmetric and asymmetric stretching vibrations of W^{6+}—O bond respectively. The bending vibrations of O—W—O bond are observed as intense band at 271 cm^{-1} and several bands of less intensity in the 200–500 cm^{-1} region. The presence of well-defined bands characteristic to WO_3 phase in the Raman spectrum of G0W600 film gives an indication of formation of WO_3 crystalline phase. The full width at half maximum (FWHM) of the symmetric stretching band at 805 cm^{-1} reflects the structural order in terms of bond length and bond angle of W—O—W [28]. The full width at half maximum (FWHM) of the symmetric stretching mode at 805 cm^{-1} obtained for this film is nearly 31.87 cm^{-1} (refer Table 1) which is close to that of the bulk sample (~30.81 cm^{-1}). Very close values of FWHM for the symmetric stretching mode around 805 cm^{-1} for G0W600 film and bulk WO_3 indicate good structural order and crystallinity of G0W600 film. The Raman spectrum of 1 wt% gold incorporated tungsten oxide film (G1W600) presents almost similar spectral features as that of pure film with the appearance of a very weak band near 922 cm^{-1}. The FWHM of the symmetric stretching band obtained at 802 cm^{-1} for G1W600 film is nearly 42.45 cm^{-1}, which is much higher than that of both bulk sample and pure film. The enhanced FWHM of this mode in G1W600 can be due to the following possibilities: i) the reduction in particle size, ii) the strain induced by gold incorporation and iii) reduction in structural order and crystallinity. The Raman spectrum of 2 wt% gold incorporated film (G2W600) presents two intense bands for the stretching modes of WO_3 phase, but the bending modes are not well-defined as in pure film. The FWHM of the Raman band corresponding to the symmetric stretching mode increases and its position shifts from 805 cm^{-1} to lower wavenumbers with increase in gold incorpora-