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Deposition of nanostructured thin films using an inductively coupled plasma chemical vapor deposition technique

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Abstract

Nanostructured materials are the fundamental building block for the realization of nanotechnology. In this work, we propose a 13.56 MHz radio-frequency (RF) inductively coupled plasma chemical vapor deposition (ICP–CVD) system for the preparation of nanostructured materials. The material we deposited is tin(IV) oxide, which has found application as the gas sensing layer in the making of miniaturized chemical gas sensors. The deposited film was characterized for its structural properties using X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). For electrical properties, four-point probe and dynamic conductance temperature measurements were performed. In this paper, we describe on our novel system as a promising candidate in the synthesis of nanostructured materials, together with the preliminary results of tin(IV) oxide deposition.

Keywords: Plasma process; Nanostructured materials; Tin oxide

1. Introduction

Nanotechnology is set to revolutionize the conventional “top-down” manufacturing approach with a new class of materials termed as nanostructured materials. The concept of manipulating and assembling atoms and molecules at nanoscale level to build macroscale substance has produced materials with unique and novel properties not previously attainable by conventional manufacturing technique. This new class of materials, often characterized by a physical dimension of 1–100 nm in at least one dimension and the presence of very high surface area has found potential application in many areas such as electronics, magnetism, optics, energy storage, electrochemistry, and biomedical sciences [1].

The controlled synthesis of nanostructured materials is vital to the success of nanotechnology where various synthesis methods have since been introduced. They can be broadly classified into physical and chemical routes. Inert gas condensation [2,3], sputtering [4,5], and high-energy ball milling [6,7] are among the examples of physical route, while chemical route includes sol–gel and precipitation technologies [8,9], electrodeposition [10,11], and chemical vapor condensation [12,13].

In this work, we propose a custom-designed inductively coupled plasma chemical vapor deposition (ICP–CVD) system as an alternative manufacturing approach for nanostructured materials. Tin oxide, one of the most studied n-type semiconductors used in the field of gas sensing was chosen as the starting coating material to establish the promise of the ICP–CVD system. Nanostructured tin oxide plays a prominent role in gas sensing where it has been reported to enhance the sensitivity and the response time of the gas sensors [14,15]. The readily compatibility of ICP–CVD with the current integrated circuits manufacturing technology is in line with the progressive development towards integrated miniaturized gas sensors with low power consumption and good reproducibility. The other advantages of ICP–CVD include independent control of ion bombardment energy towards substrate that produces different film microstructures and the opportunity to lower the deposition temperature compared to conventional atmospheric pressure chemical vapor deposition process.

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2. Experimental

The ICP–CVD system is a custom-designed thin film deposition system. A schematic diagram of the system is shown in Fig. 1. The cylindrical coil configuration is chosen for the inductively coupled plasma generation. The coil is powered at 13.56 MHz by a coaxial 2 kW RF generator that is coupled with an automatic matching network. The 4 in. substrate is placed remotely from the high-density plasma zone to achieve a clean deposition with minimized plasma damage on the substrate. The substrate temperature is maintained at the desired deposition temperature by the Eurotherm PID-controlled electrical heater mounted on the back of the substrate assembly. The advantage of independently control the ion energy offered by inductively coupled plasma has initiated the incorporation of dc-biased feedthroughs between the plasma and deposition zones for the purpose of controlling the ion extraction. Through suitable combination of dc-biased grid meshes, independent control of ion acceleration or deceleration energy is possible within the system.

A conventional bubbler delivery is being developed as the fundamental source delivery method along with an alternative path for the liquid vaporization method that promotes a more precise control of reactant source delivery. The reactant vapors can enter the chamber at two distinct inlet points, one before and another after the high-density plasma zone. The latter configuration resembles the setup of the remote plasma enhanced chemical vapor deposition where the reactant vapors do not undergo electron impact reactions as in the first configuration.

For the present study, we report on our experimental results with the most basic configuration, where the deposition was carried out without dc-biased grid meshes and the reactant vapors were introduced downstream of the plasma using the bubbler method. Commercially available dibutyltin diacetate, $(C_4H_9)_2Sn(OOCCH_3)_2$, with 98% purity was used as the metal-organic (MO) source. The liquid MO source in the bubbler was maintained at 90 °C by the Schumacher temperature control system and its vapor was transported into the chamber by ultra high purity (UHP) Ar as the carrier gas. The MO source delivery line was heated at 110 °C to prevent the condensation of the MO source in vapor phase. UHP O_2 was admitted before the high-density plasma zone where it was activated prior to the reaction with the MO source on the heated substrate.

The flow rate of Ar carrier gas and O_2 was controlled by MKS mass flow controllers (MFCs). The chamber pressure was monitored by MKS Baraton pressure gauge which forms a closed-loop pressure control with the MKS throttle valve and the MKS 152 pressure controller. An Alcatel roots pumping system exhausted the system with a base pressure of 16 mTorr. The deposition parameters used are summarized in Table 1.

Structural characterization on the deposited films was performed using X-ray diffraction (XRD) and scanning electron microscope (SEM). The XRD analysis was performed

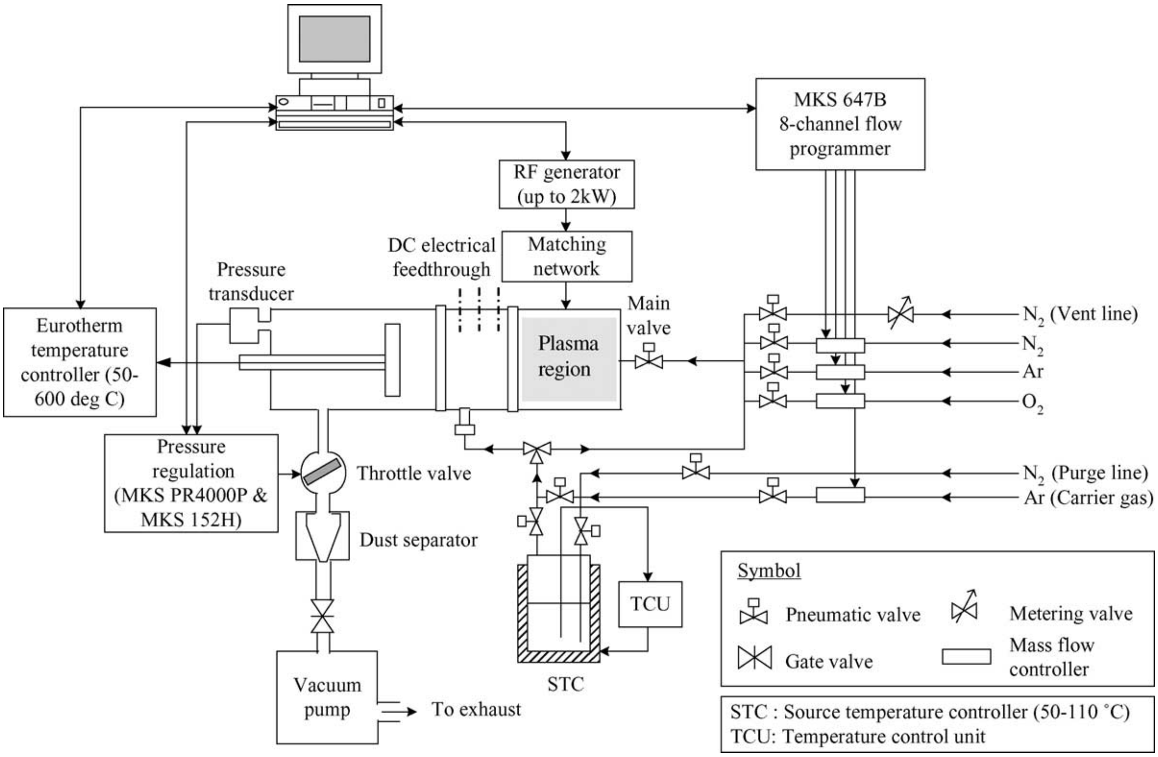

Fig. 1. A schematic presentation of the ICP–CVD system.

Table 1
Process parameters of SnO_2 deposition

Parameter	
Ar flow rate through the bubbler (sccm)	50
O_2 flow rate (sccm)	50
Substrate temperature (°C)	550
RF power (W)	1200
Deposition pressure (mTorr)	90

on a Shimadzu XRD-6000 X-ray diffractometer using Cu Kα radiation (1.5406 Å) with 2θ scan range of 20–55°. A Leo 1550 SEM was used to characterize the microstructure and morphology of the deposited films. Film thickness was accurately measured using a J.A. Wollam WVASE32 variable angle spectroscopic ellipsometer where a parameterized Lorentz oscillator model was used for the films. In electrical studies, the room temperature sheet resistance of the films was determined using the four-point probe method. The dynamic conductance temperature measurement of the samples was carried out under synthetic air flow for the temperature range of 25–300 °C.

3. Results and discussion

Fig. 2 shows the XRD diffraction pattern for the deposited film. The XRD data confirms that the sample is indeed SnO_2 (cassiterite) with tetragonal rutile structure. The film is polycrystalline in nature and the observed peaks are associated with the (1 1 0), (1 0 1), (2 0 0), and (2 1 1) planes. No peaks corresponding to SnO, Sn_2O_3, or Sn_3O_4 phases are detected from the XRD analysis. Scherrer's equation is employed to estimate the average grain size, D, along the surface normal direction:

$$D = \frac{0.9\lambda}{B\cos\theta} \qquad (1)$$

where, B is the full width at half maximum (FWHM) of the broadened diffraction line on the 2θ scale (radians), θ is the diffraction angle, and λ is the wavelength of X-rays (1.5406 Å). The calculated average grain size is 11.5 nm. As grain growth is directly associated with the substrate temperature during deposition, the grain size can be reduced by lowering the current substrate temperature at 550 °C.

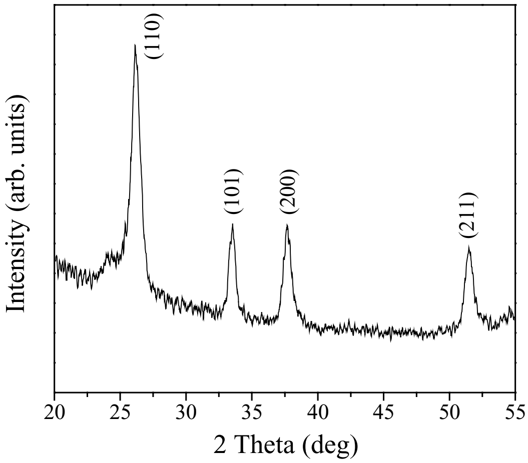

Fig. 2. The XRD patterns of the deposited SnO_2 thin films.

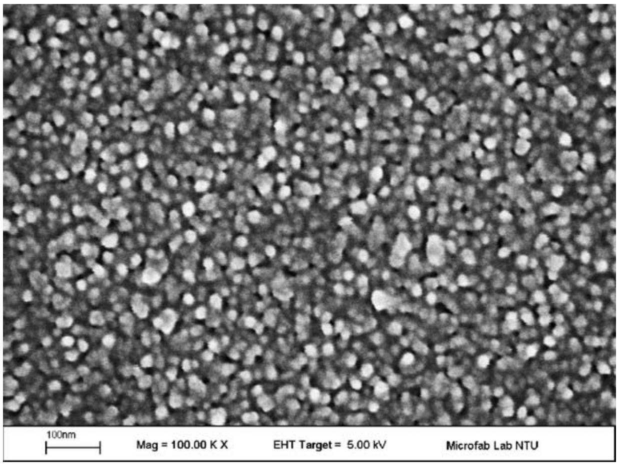

Fig. 3. SEM micrograph showing the surface morphology of the deposited SnO_2 thin film.

Fig. 3 shows the SEM micrograph of the sample with a 100,000 magnification. The micrograph exhibits a uniform and continuous distribution of spherical nano-sized grains across the film surface. The as-deposited tin oxide film has a smooth and pin-hole free surface.

The electrical property of interest is the film resistivity, for which the detection of reducing gases by semiconductor type gas sensor is based upon the conductivity change. Using the four-point probe method, the sheet resistance of the deposited film is determined as 3245 Ω. The corresponding resistivity is obtained by multiplying the sheet resistance with the film thickness derived from ellipsometer measurement. With a film thickness of 850 Å, the calculated film resistivity is $2.76 \times 10^{-2}\ \Omega\,\mathrm{cm}$. Similar film resistivity has been obtained for tin oxide thin films grown by CVD technique. Sanon et al. [16] reported film resistivity in the range of $3.9\text{–}7.7 \times 10^{-3}\ \Omega\,\mathrm{cm}$ for tin oxide deposited from $SnCl_4$.

Fig. 4 shows the dynamic conductance temperature measurement of the sample with a heating rate of 1 °C/min under synthetic air. The conductance of the sample increases with temperature and reaches its maximum at around 150 °C, which then shows a decreasing trend with the continuous increase of temperature. Below 150 °C, the sample conductance exhibits the n-type semiconductor behaviour of SnO_2. Beyond 150 °C, the oxygen starts to chemisorb on the sample surface in the form of O^- and O^{2-}, which derives electrons from the conduction band that causes the decreasing trend in the sample conductance. Similar findings has been reported by Liu et al. [17] for the ultrafine tin oxide powders prepared by PECVD.

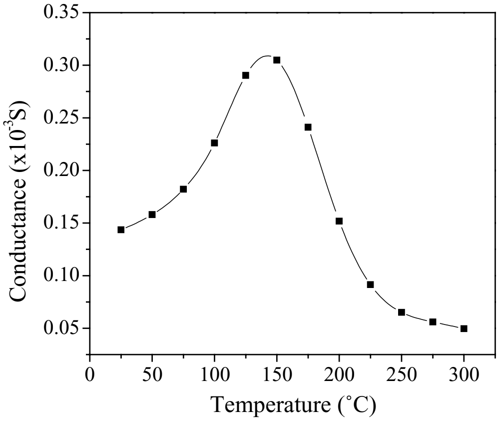

Fig. 4. Electrical conductance of the deposited film as a function of temperature.

4. Conclusions

We have described a custom-designed ICP–CVD system as an alternative processing tool in the synthesis of nanostructured materials. We have successfully deposited tin oxide thin films with uniform nano-sized grains using the most basic configuration of the novel system. With such promising results, the development of the other configurations and the influence of the various deposition parameters on the film properties will be the subject of further study to fully expand the capability of the system in nanotechnology venture.

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