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Characteristics of amorphous VO_2 thin films prepared by pulsed laser deposition

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Among the transition metal oxides, VO_2 thin films has gained considerable interest due to their reversible thermally induced semiconductor to metal phase transition around 68 °C. Based on the large change in the electrical and optical properties accompanied by such phase transition many applications can be realized. Thin films of VO_2 have been deposited by variety of techniques such as reactive sputtering [1, 2], reactive evaporation [3, 4], chemical vapor deposition [5] and solgel process [6, 7]. Recently much attention has been paid to grow VO_2 films pulsed laser deposition (PLD) technique because of its ability of growing high quality, pinhole free films at low temperatures comparing to other techniques [8]. Reports are available on pulsed laser deposition of VO_2 films under oxygen partial pressure [9–11]. Recently we reported the deposition of vanadium oxide films by pulsed laser ablation of V_2O_5 target under high vacuum [12, 13]. This article reports the properties of the VO_2 films deposited by PLD under high vacuum, which are completely different from the previous reports.

Our PLD system has been described previously [14]. Pure V_2O_5 powder (99.999%) pressed into cylindrical pellets of 13 mm diameter and 3 mm thickness was used as a target for laser ablation. A Nd:YAG laser at a wavelengths of 532 nm (pulse width: 8 ns, pulse energy: 50 mJ and pulse repetition rate: 10 Hz) was focused onto the target with a fluence of 1.2 J/cm^2. The chamber was initially evacuated to pressures as low as 1.5×10^{-6} Torr range and the film depositions were carried at the same high vacuum conditions. Deposition was done at room temperature on pyrex glass substrates kept at 45 mm away from the target. The substrate was mounted at slightly off axis with respect to the plume axis and rotated at the rate of 8 rpm during the deposition in order to get a uniform film thickness and the target is scanned continuously for uniform erosion. The film was thermally annealed at 300 °C for 90 min. The thicknesses of the films were measured as 0.15 μm using stylus profilometer (Dektak 3030). Structural analysis of both as deposited and annealed films were carried out by X-ray diffraction technique (Cu K_α radiation, Philips 1710). Temperature dependent electrical measurements were carried out by using two probe technique.

Fig. 1 shows the X-ray diffraction pattern of the vanadium oxide film deposited at the laser fluence of 1.2 J/cm^2 under high vacuum (1.5×10^{-6} Torr) shows the amorphous nature. The sheet resistance of the film was found to be 10 MΩ sq-1, which is in good agreement with the earlier report [15]. Electrical measurements were performed by mounting the samples on the temperature controlled thermal chuck. The electrical resistance of the vanadium oxide films measured as a function of temperature in the range 25 °C to 100 °C at 1 °C intervals. Fig. 2 shows the relative change in resistance as a function of temperature of the vanadium oxide film deposited in high vacuum at the laser fluence of 1.2 J/cm^2. From the figure, the semiconductor—metal transition of the resistance can be seen around 60 °C, which clearly indicates the characteristic of the VO_2 phase [16]. Such phase transitions are known to accompany change of resistance in the range of four to five orders of magnitude. In our case, it is interesting to note that the magnitude of change in resistance is very small compared to the previous reports. Width of the heating-cooling hysteresis accompanying the phase transition was found to be 10 °C. The semiconductor-metal transition occurs due the change in the crystal structure of VO_2 from monoclinic to tetragonal phase. Therefore the crystalline quality of the films plays the dominant role on the significance chance in magnitude of electrical resistance and compositional factors also influences the transition behavior [17, 18]. Based on the available literature it can be broadly categorized as the magnitude of chance in resistance by the order of 10^5 were reported for the single crystal VO_2 [16, 19, 20], order of 10^4 to 10^5 for highly oriented [3, 9, 10] and order of 10^2 to 10^3 reported for the polycrystalline [1, 6, 15, 22–28] grown on crystalline and amorphous substrates. Similarly the width of transition varies from 0.1 to 7 °C for single crystal to polycrystalline VO_2 films [1, 3, 6, 9, 10, 15, 16, 19, 20, 22–28]. Therefore, it can be inferred that the lower magnitude of the change in resistance and broad hysteresis width observed in our case may be due to the small

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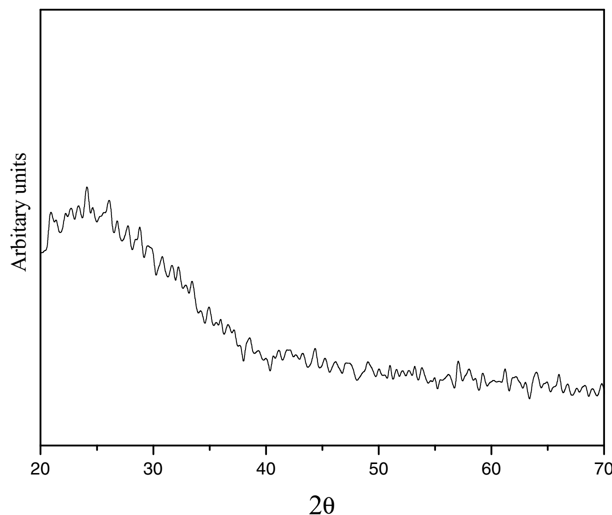

Figure 1 XRD spectrum of vanadium oxide film deposited at the laser fluence 1.2 J/cm^2.

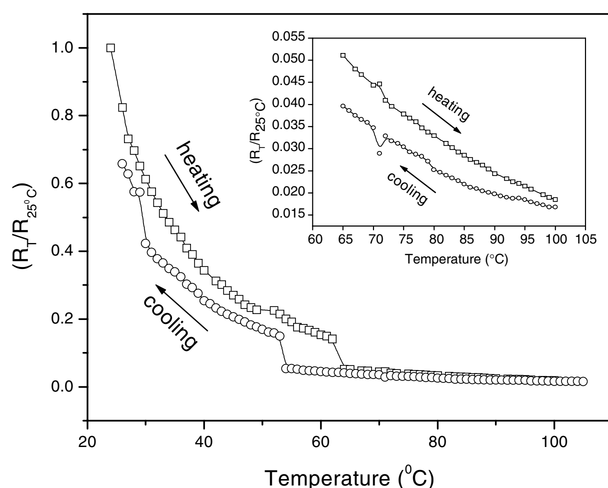

Figure 2 ($R_T/R_{25\,^\circ C}$) vs. temperature plot of the vanadium oxide film deposited at the laser fluence 1.2 J/cm^2.

crystallite size (amorphous nature of the films) [15]. From the temperature dependence resistance measurement the activation energy (E_a) determined as 0.525 eV. The temperature coefficient of resistance (TCR) is related to activation energy by TCR $= -E_a/kT^2$ (k, Boltzmann constant, T, temperature in K). The room temperature TCR is found to be 6.5% K^{-1}, which is in good agreement with the measured TCR values of pulsed laser deposited (PLD) VO_2 films [11]. On increasing the temperature above the transition temperature, a single crystal VO_2 or highly oriented VO_2 films exhibit a positive temperature coefficient of resistance, characteristics of metallic behavior [4, 10, 29, 30]. It is worthy to note that the films subjected to present study show negative temperature of resistance for the temperatures above the transition temperature (Inset Fig. 2). The presence of such negative coefficient of resistance may be due to the existence of some other semiconductor phases of vanadium oxide [15], which clearly indicates its non-stoichiometric nature. The existence of the semiconducting nature may be more likely due to deposition of V_2O_5 phase since V_2O_5 target used for ablation.

In summary, VO_2 films deposited under high vacuum by ablating V_2O_5 target. The films were studied for their structural and temperature dependent resistance properties. The film exbited sheet resistance, activation energy and TCR of 10 MΩ sq-1, 0.525 eV and 6.5% K^{-1} respectively. The low magnitude of resistance change and broad hysteresis were explained by the amorphous nature of the films. The existence of negative coefficient of resistance above the transition temperature clearly indicates the non-stoichiometric nature of the films.

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