

Synthesis and electrical properties of cubic Na_xWO_3 thin films across the metal–insulator transition

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Abstract

Highly oriented (1 0 0) Na_xWO_3 thin films were fabricated in the composition range $0.1 \leq x \leq 0.46$ by pulsed laser deposition technique. The films showed transition from metallic to insulating behaviour at a critical composition between $x = 0.15$ and 0.2 . The pseudo-cubic symmetry of Na_xWO_3 thin films across the transition region is desirable for understanding the composition controlled metal–insulator transition in the absence of any structural phase transformation. The electrical transport properties exhibited by these films across the transition regime were investigated. While the resistivity varied as T^2 at low temperatures in the metallic regime, a variable range hopping conduction was observed for the insulating samples. For metallic compositions, a non-linear dependence of resistivity in temperature was also observed from 300 to 7 K, whose exponent varied with the composition of the film.

Keywords: A. Thin films; B. Laser deposition; D. Crystal structure; D. Electrical properties

1. Introduction

Sodium tungsten bronzes (Na_xWO_3) are known to exhibit metal–insulator transition when the alkali metal concentration is lowered below $x = 0.25$ [1,2]. A weakly activated non-metallic conductivity is exhibited at lower concentrations of sodium while at higher values of x they are metallic [3]. The percolation analysis of the x dependence of conductivity performed by Lightsey [4], in the composition

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range down to $x = 0.22$, has shown that the transition from metallic to non-metallic behaviour for cubic Na_xWO_3 takes place at the critical concentration, $x_c = 0.16$. Sodium tungsten bronzes crystallize in a perovskite-like structure where the cubic lattice is thermodynamically stable for $x > 0.40$ [5]. As the cubic phase is metastable below $x \approx 0.4$, and a series of phase transformations take place at lower sodium concentrations, the direct examination of metal–non-metal transition has been proved to be difficult [6–8]. The cubic samples of Na_xWO_3 with x as low as 0.14 have been found to be superconducting by Garif’yanov et al. [9] but no information on the normal state properties has been reported.

The metal–insulator transition (MIT) was explained by Anderson localization [10] resulting from coulombic disorder generated by the randomly disposed Na^+ ions. A generalized Mott criterion for a correlation-induced MIT has also been found to be applicable for this system [11]. The transition in sodium tungsten bronzes is believed not to be driven by any structural phase transformation [10]. The investigation of MIT on Ta substituted bronzes $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$, in which the structural phase transformation is suppressed, has shown that the transition occurs for a carrier concentration ($x-y$) around 0.18 [12–14].

Since MIT in sodium tungsten bronzes is believed not to be due to structural phase transformations and the absence of cubic symmetry in Na_xWO_3 single crystals synthesized at lower sodium concentrations made the analysis difficult, thin films of Na_xWO_3 with pseudo-cubic symmetry should help in this direction. As pseudo-cubic systems can be fabricated in the form of thin films by pulsed laser deposition (PLD), it should give significant insights into the study of metal to insulator transition observed in sodium tungsten bronzes in the absence of structural phase transformation. We have earlier reported the fabrication of sodium tungsten bronzes thin films by PLD and studied their structural and electrical properties [15]. The metallic behaviour was observed up to $x \approx 0.25$. By careful preparation of the targets and the fabrication of thin films we could attain metallic behaviour to much lower sodium concentrations. We have also in this study tried to understand the electrical transport property of these thin films as they go through metallic to insulating behaviour.

2. Experimental

The thin films of sodium tungsten bronzes were prepared by pulsed laser deposition using KrF excimer laser. An energy density of 1.8–2 J/cm² and a repetition rate of 5 Hz were used on a rotating target, which was kept at a distance of 4.5 cm from the substrate. The energy density was calibrated such that for every pulse a definite thickness of the film was deposited. The targets were prepared by mixing sodium tungstate dihydrate and tungsten trioxide in the stoichiometric ratio as:



The mixture was ground thoroughly in acetone medium, pelletized and sintered in air at 630 °C for 3 days. The sodium concentration was varied in the range of x from 0.1 to 0.46 across the metal–insulator transition regime. The films were grown under vacuum with a base pressure of 10^{-5} mbar on sapphire (R -plane) substrate. The excess oxygen in the pellet should be removed by this process in order to obtain Na_xWO_3 thin films. The substrate was thoroughly cleaned with trichloroethylene, acetone and methanol and dried prior to the deposition. The optimum substrate temperature for the deposition was 550 °C and the films deposited were approximately 300 nm thick.

The growth of the thin films was characterized by a Siemens D5005 X-ray diffractometer using Cu K α radiation with Ni filter. The surface morphology was examined by JEOL 5100 LV scanning electron

microscope (SEM). The attached energy dispersive X-ray analysis unit was used to confirm the homogeneity of the films deposited. The thickness of the films deposited was confirmed using cross-sectional scanning electron microscopy. The thickness thus measured was within ± 50 Å of the expected value calculated from the deposition rates. The electrical resistivity measurements as a function of temperature were done using a standard four-probe configuration. The concentration of charge carriers of the films (for $x = 0.46, 0.25$ and 0.1) was determined by Hall measurement using the conventional Van-der Pauw technique.

3. Results

The synthesis of bulk sodium tungsten bronzes by various preparatory methods yielded cubic phase only at high sodium concentrations though the system remains metallic down to much lower sodium content. Hence, it is desirable to have cubic phases for Na_xWO_3 at low values of x . The fabrication of thin films by pulsed laser deposition technique generally facilitates the epitaxial growth of thin films. The choice of a suitable substrate should therefore help in the formation of pseudo-cubic systems. The targets used for the deposition of thin films by PLD were mixtures of the precursors thoroughly ground and heated at relatively low temperatures for long duration. The sintering temperature was kept low to avoid the loss of sodium. The non-equilibrium nature of the pulsed laser ablation process is exploited here to make thin films of Na_xWO_3 without actually using the single-phase compound as the target.

The X-ray diffraction patterns of Na_xWO_3 thin films on sapphire (*R*-plane) substrate show a highly oriented growth in the (1 0 0) direction throughout the composition range studied (Fig. 1). The diffraction peaks due to impurity phases are not observed confirming a single phase and good orientation for these films. An increase in the out-of-plane lattice parameter (a_0) value is observed with an increase in sodium concentration as can be seen from Table 1. The values obtained here are in close agreement with those obtained using Vegard's relation [2], $a_0 = 3.7846 + 0.082x$ Å. This suggests that the compositions of Na_xWO_3 thin films deposited are in accordance with the nominal compositions of their targets. The Vegard's relation holds in the range of x from 0.3 to 0.85 in bulk sodium tungsten bronzes, where the compounds crystallize in cubic symmetry. However, the out-of-plane lattice parameter values of Na_xWO_3 thin films deposited agree well with the above relation for the whole range of concentration studied. Thus, it can be assumed that the thin films grown have a cubic symmetry-like growth in the concentration region, $0.1 \leq x \leq 0.46$. The unidirectional growth of the thin films for all the compositions deposited also supports this assumption. There is a change in the colour of the films from blue ($x = 0.10$ – 0.20) to red ($x = 0.25$ – 0.46) as the sodium concentration is increased.

From the scanning electron microscopic studies, it is found that these films are composed of small particles of less than 100 nm size. Fig. 2 shows the surface morphology of $\text{Na}_{0.2}\text{WO}_3$ thin film deposited on the *R*-plane of the sapphire substrate. The films fabricated have good homogeneity as confirmed using energy dispersive X-ray analysis, within the experimental error (2%).

The variation in resistivity (ρ) with temperature, of Na_xWO_3 thin films, for different sodium compositions prepared is shown in Fig. 3. The room temperature resistivity values obtained for these films agree reasonably well with the corresponding values of the bulk solids (single crystals) for the same composition [3,4,16,17]. For example, the room temperature resistivity of Na_xWO_3 thin films for $x = 0.46, 0.33$ and 0.25 are 81, 157 and 346 $\mu\Omega$ cm, respectively. The corresponding values for the single crystals reported in the literature are 70, 238 and 804 $\mu\Omega$ cm. Though the values obtained are comparable

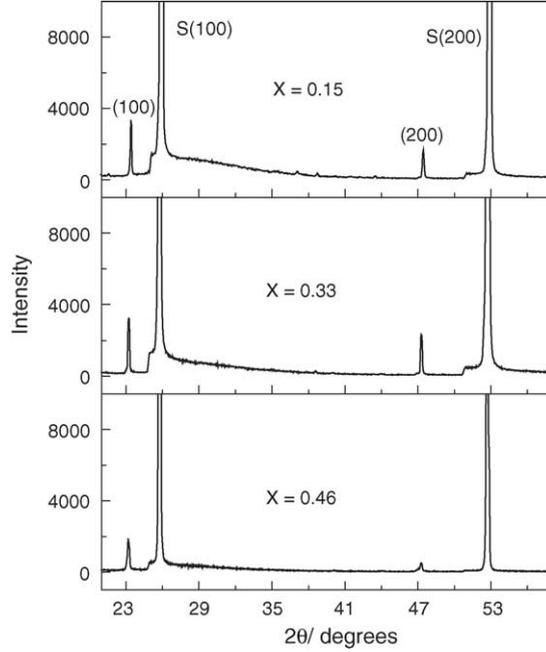


Fig. 1. The X-ray diffraction pattern of Na_xWO_3 thin films on sapphire (*R*-plane) substrate for $x = 0.15, 0.33$ and 0.46 . ‘S’ in the figure denotes the substrate.

at higher sodium concentrations, at low sodium content the room temperature resistivity of Na_xWO_3 thin films is much lower than the corresponding values reported for the bulk solid. The decrease in the resistivity of the thin films at lower x should be due to their pseudo-cubic symmetry when grown on appropriate substrate as against tetragonal or monoclinic distortions observed for bulk solids. The conduction pattern of the thin films changes from metallic to semiconducting behaviour around $x \sim 0.15$.

Fig. 4 shows the gradual increase in the resistivity of Na_xWO_3 thin films with a decrease in sodium concentration at various temperatures measured. Since every sodium atom contributes one electron to the conduction band of sodium tungsten bronzes, the number of charge carriers increases with increase in the level of sodium doping resulting in the decrease of the resistance. The increase in charge carriers (electrons) with increase in x is confirmed by the Hall measurements. $\text{Na}_{0.46}\text{WO}_3$ thin films are found to have a charge carrier concentration of $0.88 \times 10^{22} \text{ cm}^{-3}$ using a free electron approximation, which

Table 1
Out-of-plane lattice parameter of Na_xWO_3 thin films on the sapphire (*R*-plane) substrate

Composition (x)	Out-of-plane lattice parameter (\AA)
0.46	3.835 (1)
0.33	3.828 (2)
0.25	3.812 (3)
0.20	3.805 (3)
0.15	3.797 (2)
0.10	3.792 (2)

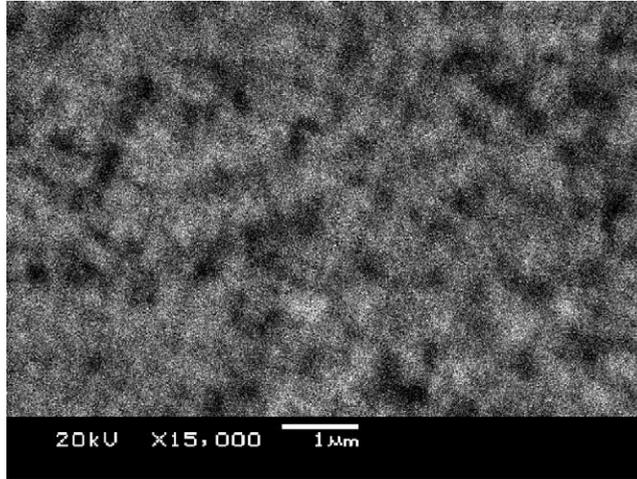


Fig. 2. SEM image of $\text{Na}_{0.2}\text{WO}_3$ thin film grown on sapphire (*R*-plane) substrate.

is close to the value of $1.1 \times 10^{22} \text{ cm}^{-3}$ in the corresponding single crystal [5,18]. The carrier concentration decrease from $0.45 \times 10^{22} \text{ cm}^{-3}$ at $x = 0.25$ to $0.27 \times 10^{22} \text{ cm}^{-3}$ at $x = 0.15$. The variation in the carrier density is in accordance with the observed values for the corresponding bulk compounds.

There is little variation in resistivity of the films at low temperatures (below 30 K) in the metallic region as can be seen from the electrical measurements. The residual resistivity (ρ_0) obtained by extrapolating the data to 0 K also shows a gradual decrease in the value with increasing sodium concentration. The resistivity shows a T^2 dependence on temperature in the metallic samples below 50 K. However, above 75 K ρ varies linearly with temperature, which is due to the interaction of electrons with the lattice vibrations. A non-linear behaviour (T^n) is observed in the temperature dependence of resistivity over the region from 300 to 7 K. The value of the exponent (n) lies between

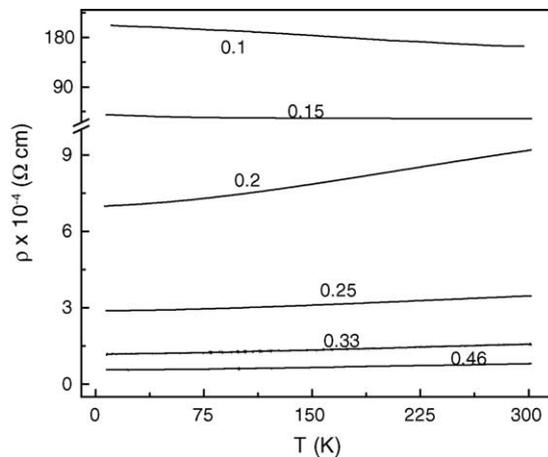


Fig. 3. Resistivity as a function of temperature for Na_xWO_3 thin films in the composition range, $x = 0.1\text{--}0.46$.

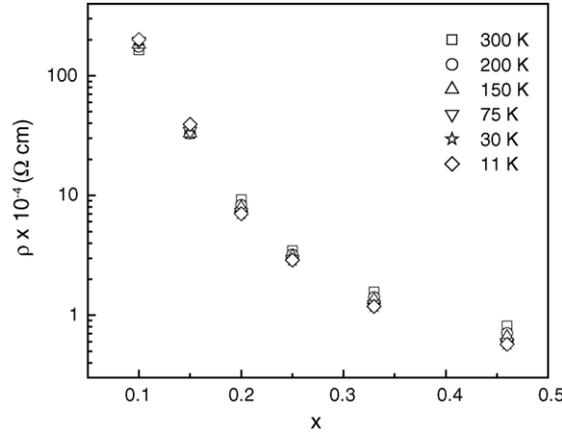


Fig. 4. The semi-log plot of resistivity as a function of sodium concentration at various temperatures for Na_xWO_3 thin films.

1.2 and 1.5 in these samples. Fig. 5 shows the conduction behaviour at various temperature regions for $x = 0.33$.

In the semiconducting samples, the conduction at low temperature shows Mott's variable range hopping mechanism [19] and the relation is satisfied for the hopping exponents $1/4$, $1/3$ and $1/2$. However, the fitting is best for $\ln \sigma$ (σ is the conductivity) versus $T^{-1/4}$ coordinates. At high temperatures, the conduction behaviour could be explained by the thermally activated transport of Arrhenius type.

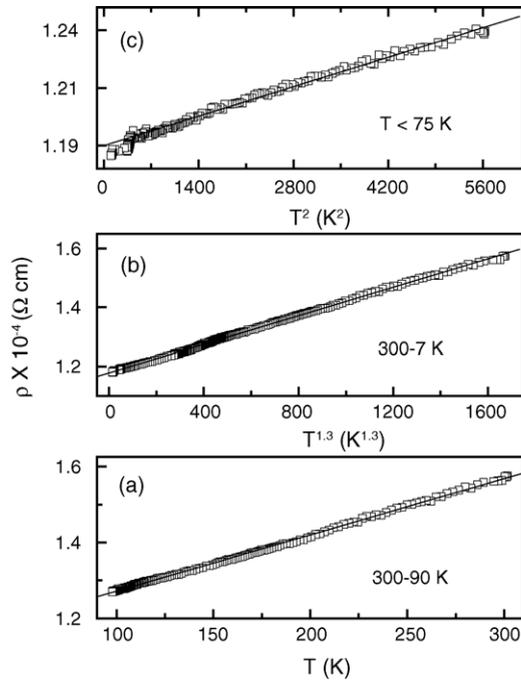


Fig. 5. Temperature dependence of resistivity of $\text{Na}_{0.33}\text{WO}_3$ thin film: (a) linear at high temperatures, (b) non-linear in the temperature range 300–7 K and (c) varies as T^2 at low temperatures.

4. Discussion

The direct observation of MIT has been difficult in bulk Na_xWO_3 since the system undergoes a series of structural transformations and the transition is believed not to be caused by any structural phase change. Investigation of MIT on tantalum substituted Na_xWO_3 assumed significance mainly due to the absence of structural changes in the system on varying the sodium content. Various models including those of Anderson–Mott–Hubbard [20,21] and the percolation approach [3,4] have predicted semi-conducting behaviour for Na_xWO_3 below a certain critical sodium concentration. The transition point was predicted to be $x_c = 0.18$ and 0.16 , respectively, by Anderson–Mott–Hubbard and the percolation models.

Since the deposited films have a pseudo-cubic symmetry, the structural changes expected at low values of x are suppressed making Na_xWO_3 a suitable system for studying the metal–insulator transition. By forcing the real lattice with randomly intercalated sodium atoms into a near perfect perovskite structure, the effect of structural disorder can be minimized. We have observed the transition from metallic to insulating behaviour in Na_xWO_3 thin films with the critical concentration falling in the region $0.15 < x < 0.2$.

The conductivity of sodium tungsten bronzes depends on the area of the Fermi surface (Σ) and the average mean free path at the Fermi surface (λ). If every sodium atom is assumed to contribute one electron to the conduction band, then the area of the Fermi surface will increase with increasing sodium concentration. As both Σ and λ increase with increasing sodium concentration, the conductivity also increases. The contribution to the residual resistivity from lattice imperfections and impurities is assumed to be small since the resistivity at different temperatures has strong non-linear x dependence in Na_xWO_3 thin films. Hence, the major contribution to the residual resistivity would be from the electron–sodium vacancy scattering apart from the effects due to the substrate lattice. As the sodium vacancy decreases with increase of x , the resistivity decreases.

At high temperatures, the resistivity of a metal, due to the interaction of the electron with the lattice vibrations, is given by,

$$\rho \propto \frac{T}{M\theta^2} \quad (2)$$

where M is the mass of the electron, T the absolute temperature and θ is the Debye temperature [22,23]. This linear behaviour is observed above 75 K in Na_xWO_3 thin films in the metallic region. Below this temperature, the resistivity varies as T^2 indicating the electron–electron interaction present in the system. We have also observed a non-linear dependence of resistivity on temperature in the region from 300 to 7 K in the metallic samples. The non-linear behaviour of resistivity over a wide range of temperature is reported in the literature for various oxide systems, including those of overdoped superconducting materials [24–26]. This behaviour can be due to the coexistence of electron–phonon and electron–electron interactions present in the system.

In the non-metallic region, two forms of conduction are mainly observed. At high temperatures, the thermal dependence of conductivity shows Arrhenius-like behaviour which is expected of a heavily doped semiconductor. The low temperature region shows variable range hopping from one localized state to another. Though the exponent $1/4$ at low temperatures is considered when electron–electron interactions are neglected, the deviations observed predict the presence of these interactions.

5. Conclusion

We have been able to fabricate highly oriented Na_xWO_3 thin films on sapphire (*R*-plane) substrate, with a pseudo-cubic symmetry, for various compositions across the metal–insulator transition regime. The non-equilibrium nature of the pulsed laser ablation process has been exploited in preparing these non-stoichiometric oxide thin films. The critical composition at which the transition is observed lies in the composition region $0.15 < x < 0.2$, which agrees well with the theoretical predictions on this system. The cubic-like symmetry of Na_xWO_3 thin films would be helpful in studying the MIT in the absence of structural phase transformation. The coexistence of electron–electron and electron–lattice interactions is revealed by the non-linear dependence of resistivity on temperature in the metallic compositions. The conduction at low temperature occurs by the variable range hopping between localized states in the non-metallic region.

Acknowledgement

The authors gratefully acknowledge the financial assistance from the Department of Science and Technology, Government of India, New Delhi.

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