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STRUCTURE AND PROPERTY OF HETEROEPITAXIAL TiO$_2$/VO$_2$ MULTILAYERS*

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Abstract

Various types of TiO$_2$/VO$_2$ multilayer structures have been prepared on sapphire ($1\bar{1}20$) substrates by a low-pressure metal-organic chemical vapor deposition process. X-ray diffraction and transmission electron microscopy techniques were used to study the crystallinity and epitaxial relationships of the deposited films. High resolution electron microscopy was used to examine the microstructure of the overlayers and interfaces. Electrical resistivity measurements were performed to investigate the metal-semiconductor phase transition of VO$_2$ layers in multilayer structures.

Introduction

Thin oxide films in the form of single-crystal, as opposed to amorphous or polycrystal, are required or at least preferred for many potential technological applications [1-5]. In some cases [5], one needs to layer a few different oxide materials together on the same substrate not only in single-crystal form but also in controlled crystallographic orientations. Research in this area is in its infancy [6].

In our recent work [7], we selected titanium and vanadium oxide systems to study the growth of epitaxial films in the metal-organic chemical vapor deposition (MOCVD) process. Single-crystal films of TiO_2 and VO_2 have been successfully obtained on sapphire (α-Al_2O_3) substrates with various surface orientations and seven distinct epitaxial relationships have been observed [7].

A crystal of VO_2 will undergo a phase-transition, which involves only a slight shift of cations relative to anions, from low temperature monoclinic phase to high temperature tetragonal phase at approximately 340 K [8,9]. The tetragonal phase of VO_2 has the rutile-structure and its lattice constants are fairly close to that of rutile TiO_2. Therefore, it is conceivable that high quality multilayer or superlattice structures made of TiO_2 and VO_2 may be achievable under appropriate conditions. In this work, various types of TiO_2/VO_2 multilayer structures have been fabricated and characterized.

Experimental

The films were grown in a cold-wall horizontal low-pressure MOCVD system. Detailed description of the apparatus and the sample preparation procedure has been given elsewhere [10]. Various double-layer, sandwich, and superlattice structures have been fabricated. In the case of superlattice structure, we always grew a buffer layer of rutile TiO_2, approximately 30 nm in thickness, on top of the substrate surface prior to the subsequent deposition of superlattice. The substrate used in this study is sapphire $(1\bar{1}20)$.

X-ray diffraction study of the films was performed using a Rigaku X-ray diffractometer and a Huber four-circle diffractometer. Both diffractometers were equipped with a rotating anode with Cu Kα radiation. Transmission electron microscopy (TEM) and high resolution electron microscopy (HREM) were employed to study the microstructures of the films and the interfaces. Resistance of the film was measured by an a-c signal at 10 kHz and 100 mV using an HP 4192A Impedance Analyzer. Electrical contact was made with indium solder.

Results and Discussion

Single-layer TiO_2 and VO_2 films grown on sapphire $(11\bar{2}0)$ have been studied in detail [7,10]. Within a wide range of growth conditions, the epitaxial relationships between the rutile TiO_2 (R), monoclinic VO_2 (V), and sapphire substrates (S) have been determined, by both X-ray and TEM, to be $(101)[010]_R//(11\bar{2}0)[0001]_S$ and $(200)[010]_V//(11\bar{2}0)[0001]_S$. All the samples studied in this work follow these epitaxial relationships.

A double-layer film was prepared by growing TiO_2 at 800°C for 30 min and then VO_2 at 500°C for 20 min. The thicknesses of TiO_2 (bottom layer) and VO_2 (top layer) are 200 and 150 nm, respectively. X-ray θ–2θ scan data of this sample are shown in Fig. 1. In addition to the substrate peak, which is off-scale due to its strong intensity, the two film peaks at $2\theta = 36.12$ and 37.2° correspond well to the rutile (101) and VO_2 (200) reflections, respectively. φ scans of this sample were performed in the four-circle diffractometer and the result has shown that the epitaxial relationship follows those in the single-layer configuration, i.e., $(200)[010]_V//(101)[010]_R//(11\bar{2}0)[0001]_S$. A good number of samples have been fabricated in various types of double-layer and sandwich configurations and they all show the above epitaxial relationship. Figure 2(a) shows the cross-sectional TEM micrograph of a double-layer film with a ~33 nm bottom layer of TiO_2 (grown at 800°C) and ~115 nm top layer of VO_2 (grown at 500°C). The TiO_2/VO_2 interface looks flat at this magnification. A further magnified high resolution image of a part of the interface is shown in Fig. 2(b). As can be seen, the interface is

coherent and shows no misfit dislocation. However, the interface roughness is in the order of a few nm.

In superlattice configuration, we have prepared three samples with different modulation lengths. The three samples all consist of a ~30 nm TiO_2 buffer layer (grown at 800°C) and, on top of that, 40 layers of alternating VO_2 and TiO_2 (20 layers for each, grown at 750°C). The growth conditions for the three samples are the same except for the deposition time. The deposition cycling times for the three samples, designated as A, B, and C, were 1 min/1 min, 5 min/5 min, and 10 min/10 min, respectively. It should be mentioned that the growth rates of TiO_2 and VO_2 are different. At this point, we do not know the thicknesses of individual layers of TiO_2 and VO_2. But they may be quite different although the deposition time for the two constituent materials is the same. The X-ray θ–2θ scan data of sample A, B, and C are shown in Fig. 3(a), (b), and (c), respectively. Note that data for sample A (Fig. 3(a)) show one strong diffraction peak located at $2\theta = 36.4°$. Data for sample B also show one diffraction peak but the line width (full width at half maximum or FWHM) of this peak are substantially larger than that for sample A (FWHM = 0.5° in Fig. 3(b) as compared to 0.2° in Fig. 3(a)). Data for sample C show two diffraction peaks located at $2\theta = 36.25$ and 36.91°. One possible explanation for these data is that, at the growth temperature of 750°C, there was severe atomic interdiffusion between TiO_2 and VO_2 during deposition. In the case of sample A, because both TiO_2 and VO_2 individual layers were so thin that the atomic mixing between them was thorough and uniform and the resulting film was therefore a solid solution $Ti_xV_{1-x}O_2$. This solid solution film still possesses rutile structure but its lattice constants are between that of rutile TiO_2 and tetragonal VO_2 and, therefore, the X-ray diffraction peak ($2\theta = 36.4°$) appears between 36.1° and 37.2°. For sample B, since the individual layers are thicker, the atomic mixing is not uniform. The diffraction peak is broad, indicating a distribution of atomic spacing. As for sample C, which consists of the thickest individual layer, substantial parts of TiO_2 and VO_2 (away from the interface) remain only slightly mixed with each other and they yield diffraction peaks ($2\theta = 36.25°$ and 36.91°) close to that of pure TiO_2 and VO_2 ($2\theta = 36.1°$ and 37.2°).

In order to further investigate the above speculation, we have grown a superlattice at a much lower temperature to see whether atomic intermixing effect can be minimized. The sample consists of 20 layers of alternating TiO_2 and VO_2 (10 layers for each, grown at 500°C) on top of a buffer layer of TiO_2 (~28 nm in thickness, grown at 800°C). The thicknesses of individual layers of TiO_2 and VO_2 are about 14 and 5 nm, respectively. The X-ray θ-2θ scan data of this sample are shown in Fig. 4. The diffraction spectrum looks very similar to that of sample C. The electron diffraction pattern and the cross-sectional TEM micrograph of this sample are shown in Fig. 5(a) and (b), respectively. A number of weak superlattice spots between the bright substrate spots can be seen in the diffraction pattern, indicating a reasonably good periodic structure due to the presence of alternating layers of TiO_2 and VO_2.

From the TEM data shown in Fig. 2 and 5, it does not look like there is severe atomic intermixing at the TiO_2/VO_2 interfaces when the samples were grown at 500°C. If indeed there is no or little atomic intermixing at the interfaces, then, to explain the peak shifts in Fig. 4, it is possible that the shifts of the X-ray diffraction peaks are due to strain in the individual layers rather than solid solution mixing. However, in order to explain the strain effect on the X-ray diffraction peak shifts (i.e., atomic plane d spacing change), our TiO_2/VO_2 interface has to be a rough one. Figure 6 schematically shows a rough TiO_2/VO_2 interface. As shown in the figure, interface consists of vertical and horizontal parts. Since the lattice constants of rutile TiO_2 (a = 4.594 Å, c = 2.959 Å) are slightly larger than that of tetragonal VO_2 (a = 4.54 Å, c = 2.88 Å), the atomic plane matching along the horizontal part of interface tends to decrease the d spacing of VO_2 (200) and increase the d spacing of TiO_2 (101). This would shift the rutile (101) peak toward smaller 2θ value and VO_2 (200) peak toward larger 2θ value which would contradict our experimental results. On the other hand, the atomic plane matching along the vertical part of interface will do the opposite and shift the two peaks (2θ = 36.1° and 37.2°) toward each other which is what we observed. The effect of vertical matching may dominate in the case of rough interfaces. For the same reason, this type of strain in TiO_2 and VO_2 layers can also explain the X-ray data of the 750°C superlattice (Fig. 3).

Resistance vs. temperature (R-T) measurements were performed on the superlattice samples to study the metal-semiconductor phase transition for those thin layers of VO_2. Figure 7(a) shows the R-T curve obtained from a typical single-layer VO_2 film (unstrained). As shown, the transition curve is very much like that of a bulk VO_2 crystal: a four orders of magnitude change in resistance, and sharp transition at about 336 K. The R-T curve of sample C (10 min/10 min superlattice) is shown in Fig. 7(b). Interestingly, the transition temperature shifts rather substantially to about 300 K and there is only a two orders of magnitude change in resistance. The R-T curve of sample A (1 min/1 min superlattice) is shown in Fig. 7(c). There is hardly any "transition" that can be seen over the entire temperature range (100 to 400 K). Whether the absence of phase-transition is due to finite size or strain effect or atomic mixing is not clear at this point.

Conclusion

Various types of TiO_2/VO_2 multilayer structures have been prepared by the MOCVD technique. The epitaxial relationships in these multilayer configurations follow those observed in single-layer films. The TiO_2/VO_2 interface roughness is typically in the order of nm. Superlattice was successfully obtained if individual layer thickness is greater than approximately 10 nm. TiO_2 and VO_2 layers are possibly highly strained or intermixed in the superlattice configuration. It is interesting to note that the strain or the mixing of TiO_2 in VO_2 layer can drastically change the behavior of metal-semiconductor transition.

References

[1]   H. L. Glass and J.H.W. Liaw, J. Appl. Phys. 49 (1978) 1578.

[2]   E. Yamaka, H. Watanabe, H. Kimura, H. Kanaya and H. Ohkuma, J. Vac. Sci. Technol. A 6 (1988) 2921.

[3]   M. H. Francombe and S. V. Krishraswamy, J. Vac. Sci. Technol. A 8 (1990) 1382.

[4]   Y. Kobayashi, S. Terada and K. Kubota, Thin Solid Films 168 (1989) 133.

[5]   L. A. Weller-Brophy, B.J.J. Zelinski and D. P. Birnie III, Mater. Res. Soc. Bull 14(4) (1990) 25.

[6]   E. G. Bauer, B. W. Dodson, D. J. Ehrlich, L. C. Feldman, C. P. Flynn, M. W. Geis, J. P. Harbison, R. J. Matyi, P. S. Peercy, P. M. Petroff, J. M. Phillips, G. B. Stringfellow and A. J. Zangwill, J. Mater. Res. 5 (1990) 852.

[7]   H.L.M. Chang, H. You, J. Guo and D. J. Lam, Appl. Surf. Sci. 48-49 (1991) 12.

[8]   R.W.G. Wyckoff, "Crystal Structures," Vol. 1, 2nd ed., Interscience, New York, 1965.

[9]   G. Anderson, Acta Chem. Scand. 10 (1956) 623.

[10] H.L.M. Chang, H. You, Y. Gao, J. Guo, C. M. Foster, R. P. Chiarello, T. J. Zhang and D. J. Lam, J. Mater. Res. (1992) in press.

Figure Captions

1. X-ray θ–2θ scan data of a double-layer film which consists of a VO_2 layer (150 nm) on top of a TiO_2 layer (200 nm) grown on sapphire $(11\bar{2}0)$ substrate.

2. (a) Cross-sectional TEM micrograph of a $VO_2/TiO_2/Sa(11\bar{2}0)$ double-layer film; (b) HREM image of a part of the VO_2/TiO_2 interface.

3. X-ray θ–2θ scan data of sample A(a), B(b), and C(c).

4. X-ray θ–2θ scan data of a TiO_2/VO_2 superlattice.

5. (a) Electron diffraction pattern and (b) cross-sectional TEM micrograph of the sample of Fig. 4.

6. Schematic of a rough TiO_2/VO_2 interface.

7. Resistance vs. temperature curves for (a) a typical single-layer single-crystal VO_2 film, (b) sample C, and (c) sample A.
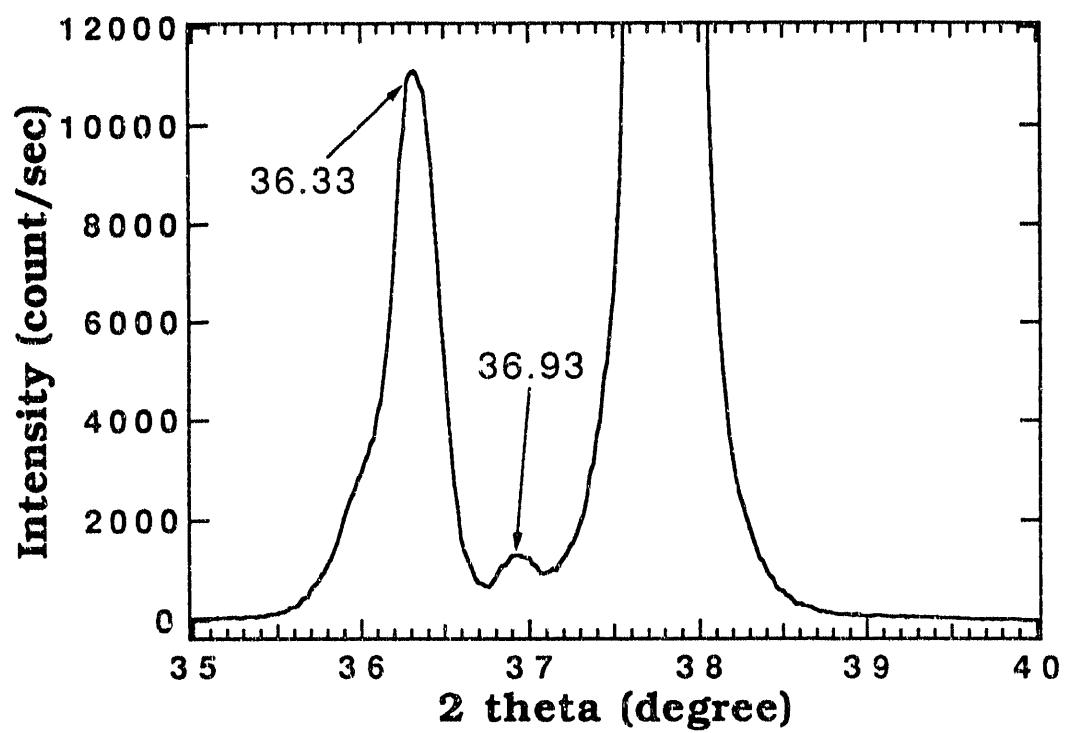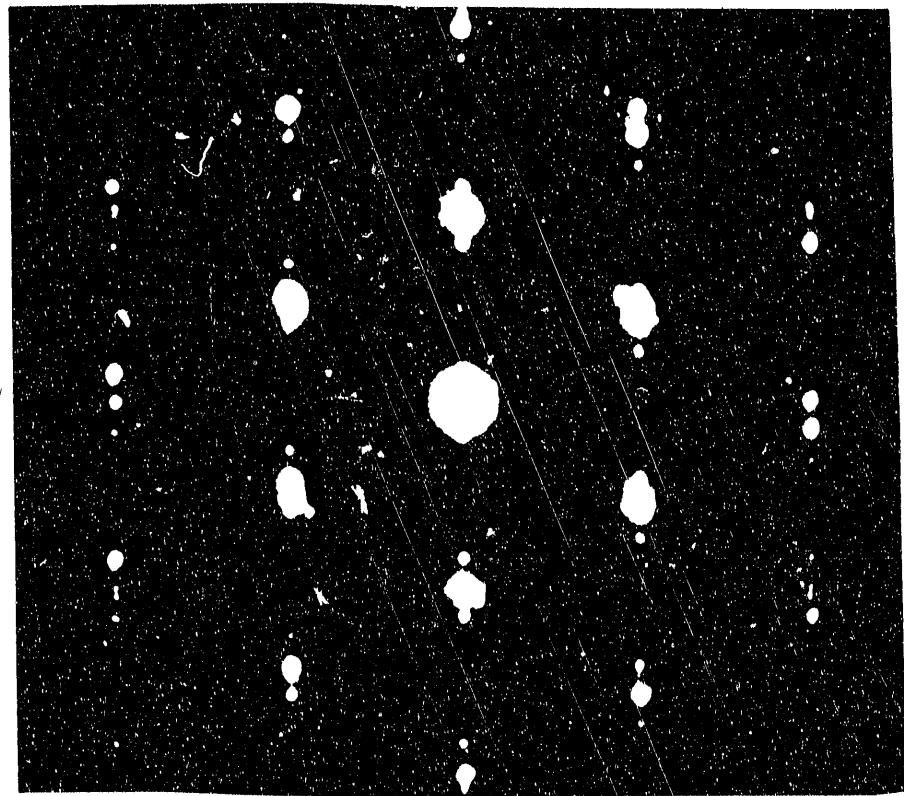
Fig. 1

Al₂O₃

VO₂

TiO₂

2 nm
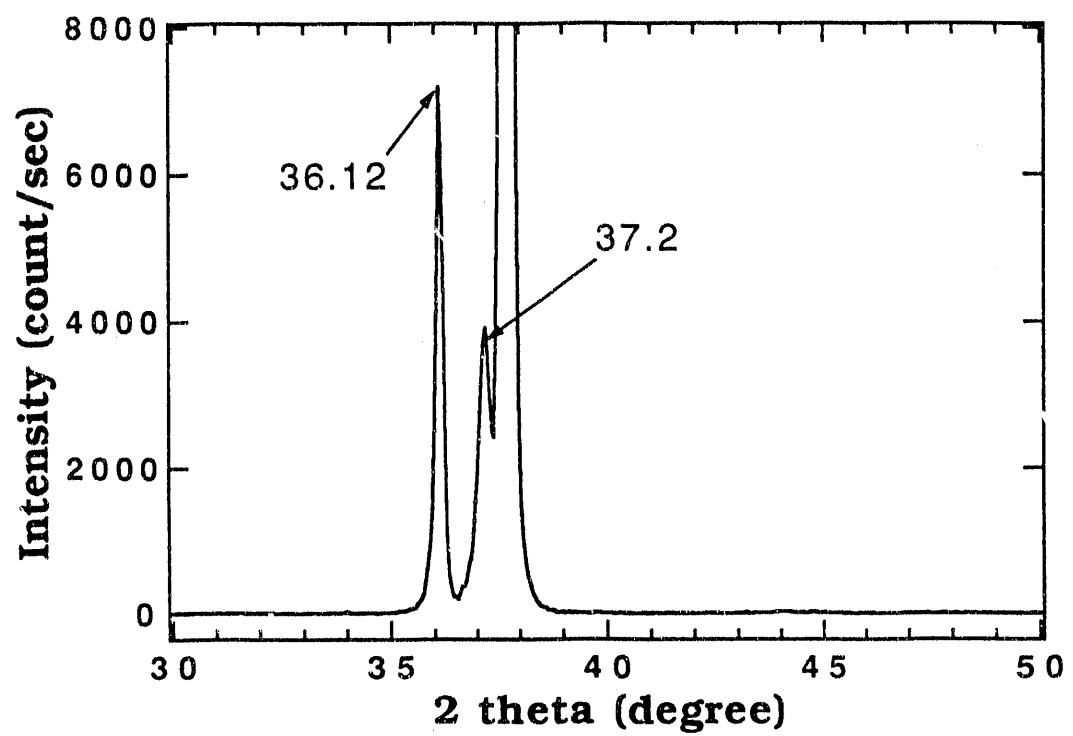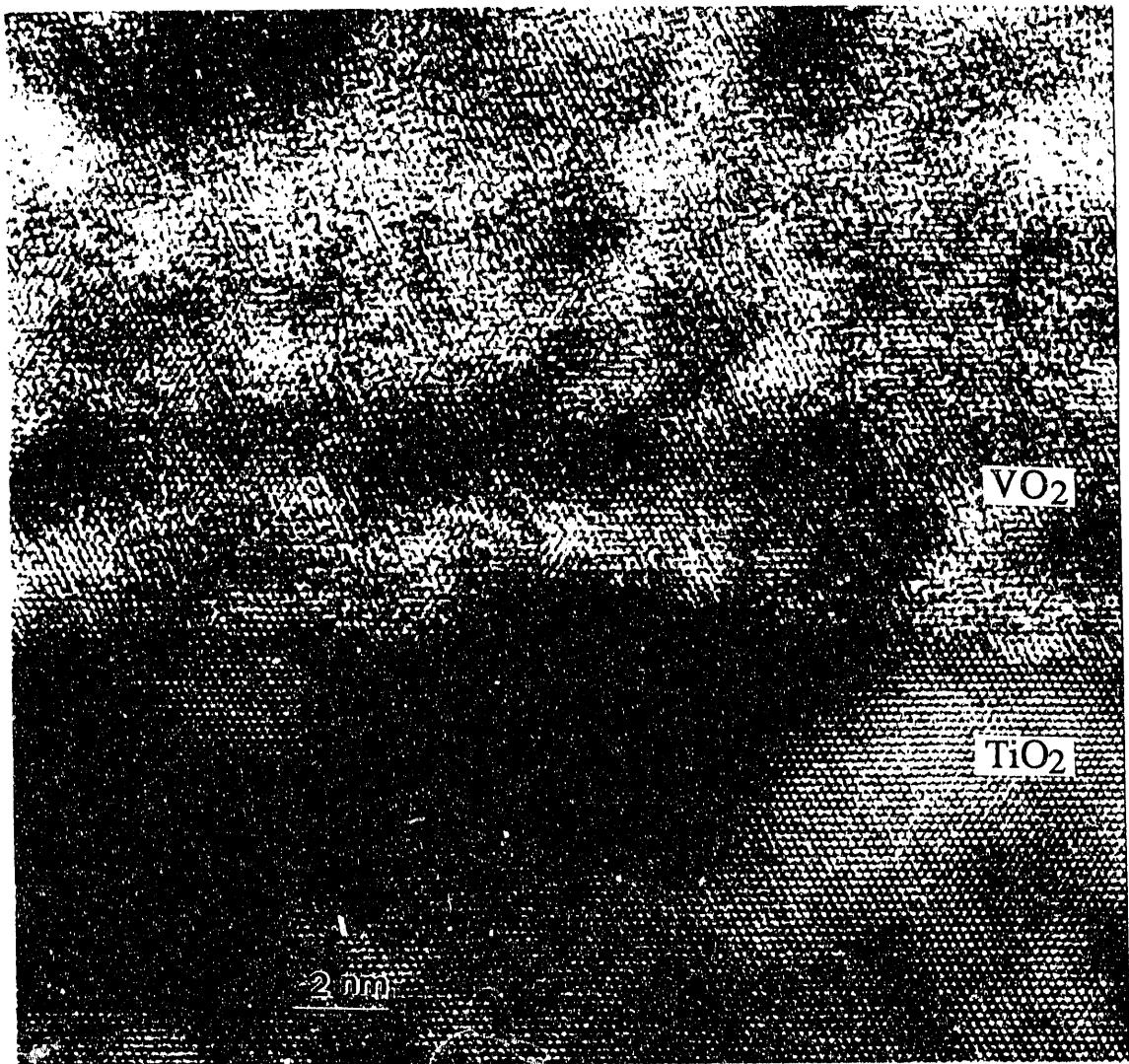
Fig. 2 (b)
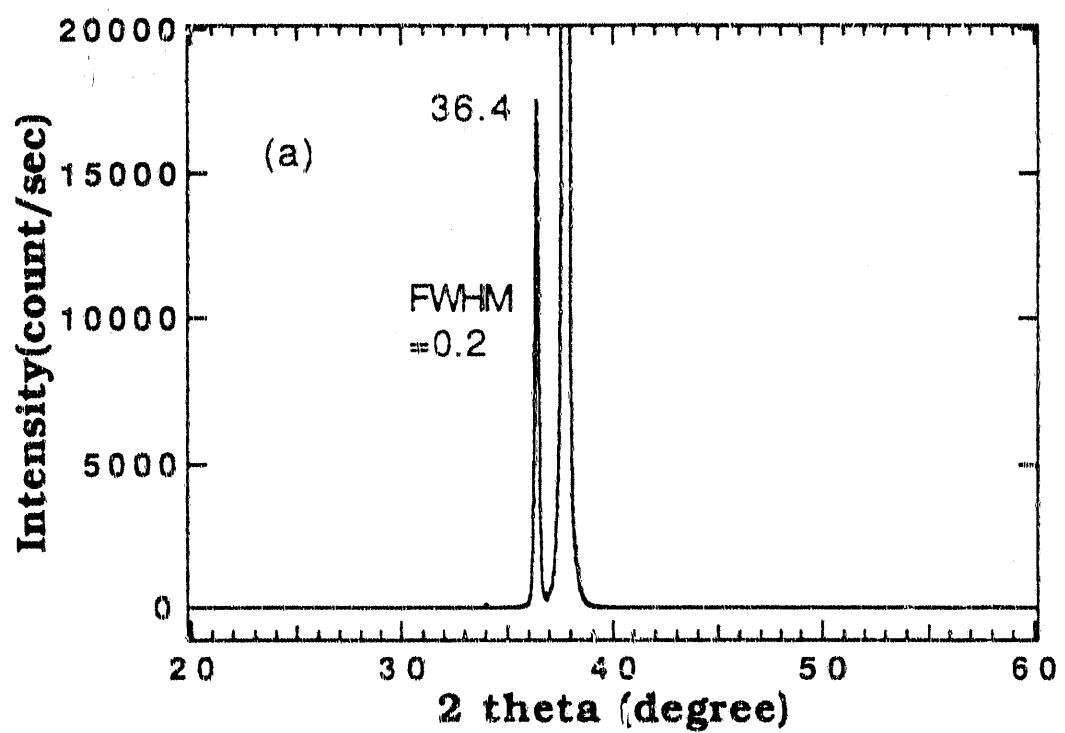
Fig. 3(a)
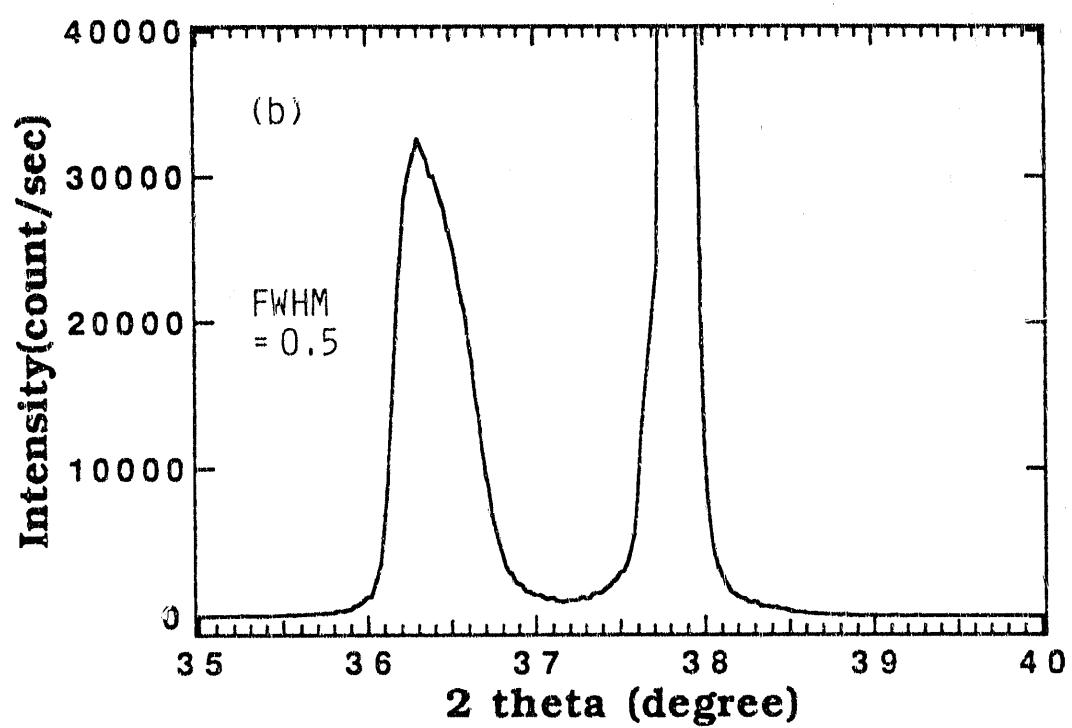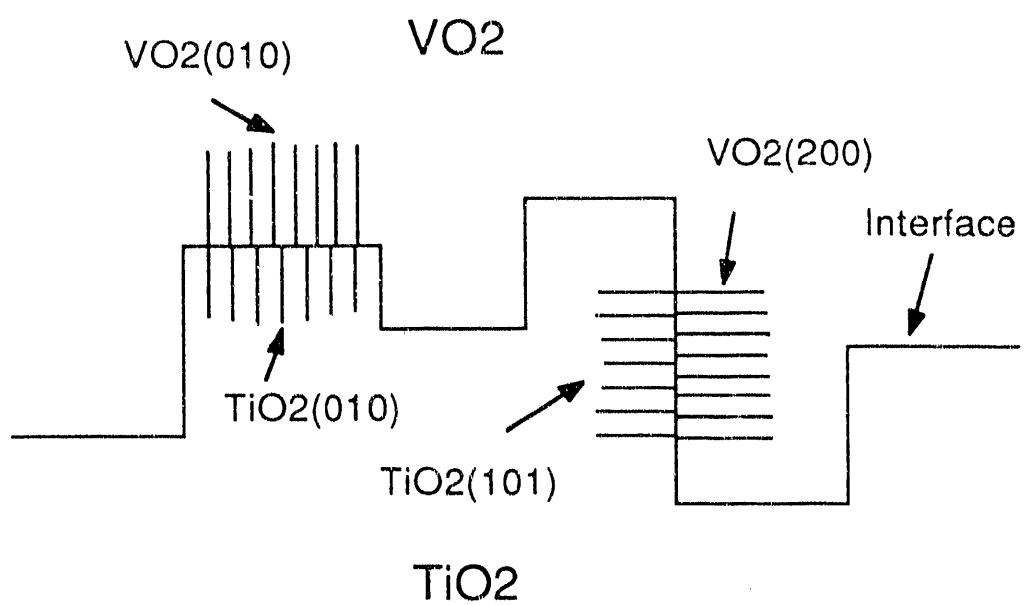
Fig. 3 (b)
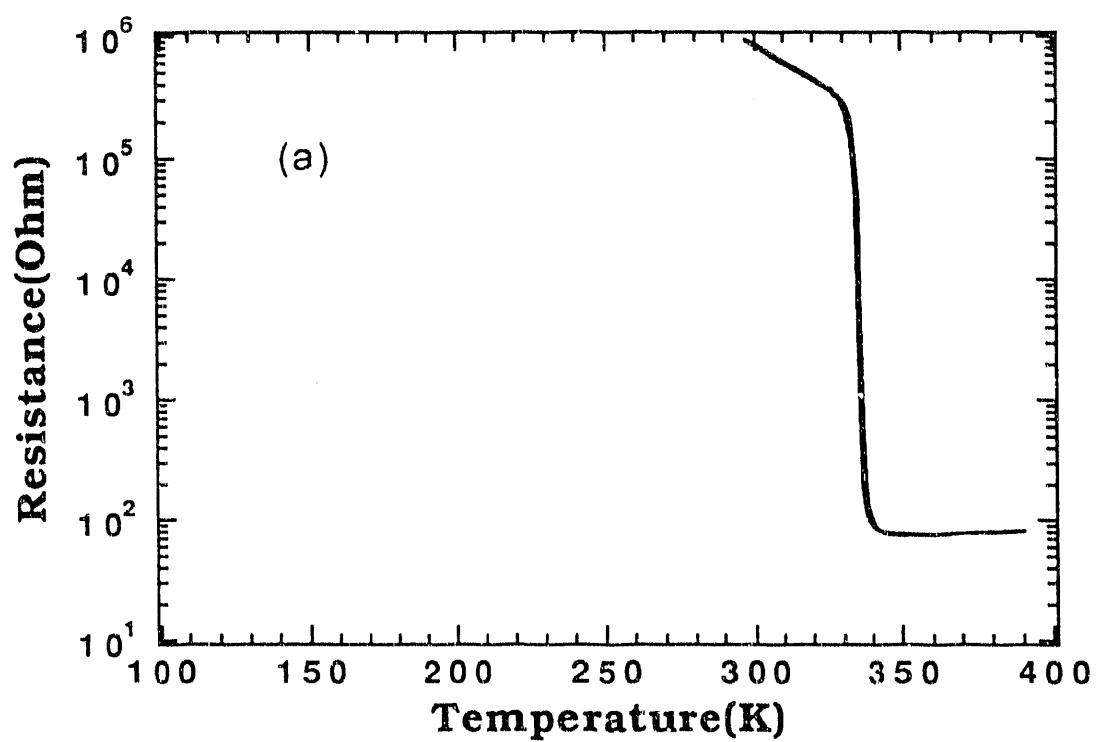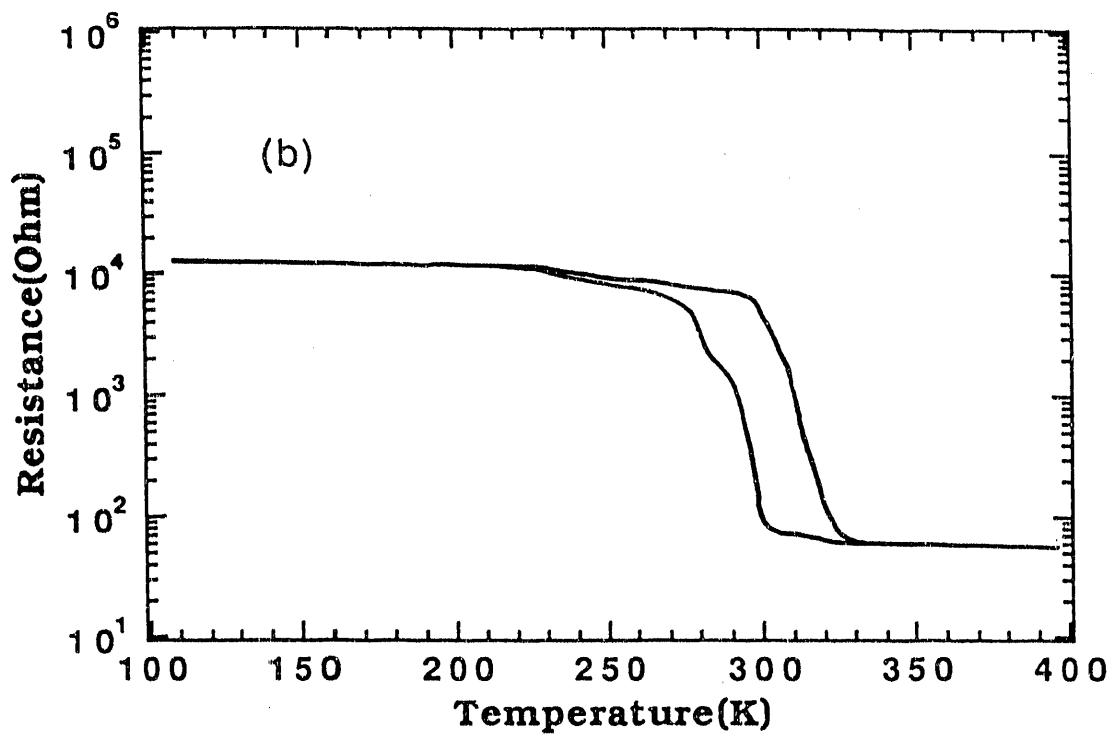
Fig. 3(c)

Fig. 4

Fig 5(a)

TiO$_2$/VO$_2$

Al$_2$O$_3$
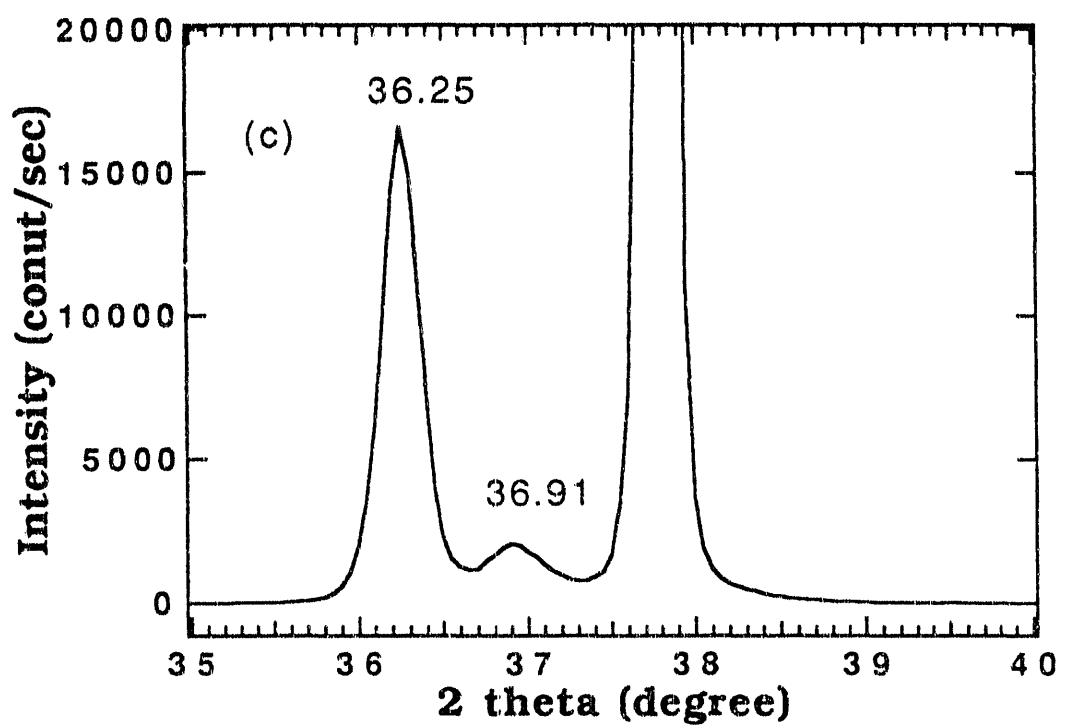
25 nm

Fig. 6

Fig. 7(a)

Fig. 7 (b)
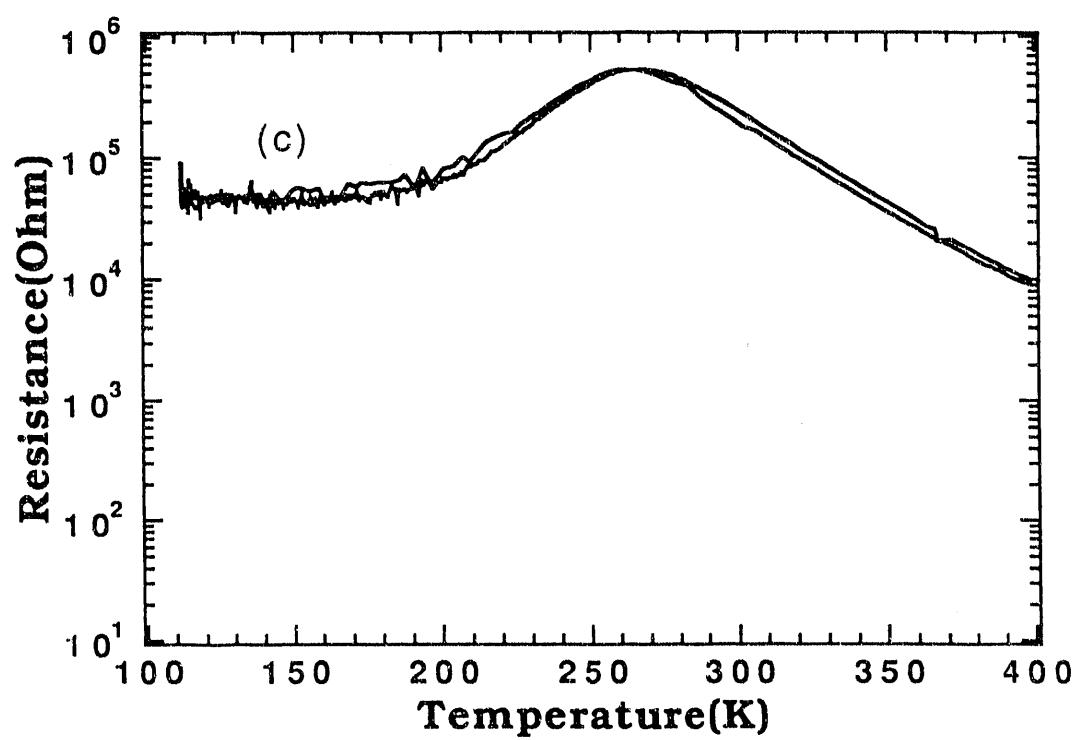
Fig. 7(C)

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