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## Thin film bi-epitaxy and transition characteristics of TiO<sub>2</sub>/TiN buffered VO<sub>2</sub> on Si(100) substrates

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### ABSTRACT

Bi-epitaxial VO<sub>2</sub> thin films with [011] out-of-plane orientation were integrated with Si(100) substrates through TiO<sub>2</sub>/TiN buffer layers. At the first step, TiN is grown epitaxially on Si(100), where a cube-on-cube epitaxy is achieved. Then, TiN was oxidized in-situ ending up having epitaxial r-TiO<sub>2</sub>. Finally, VO<sub>2</sub> was deposited on top of TiO<sub>2</sub>. The alignment across the interfaces was established as VO<sub>2</sub>(011) || TiO<sub>2</sub>(110) || TiN(100) || Si(100) and VO<sub>2</sub>(110) / VO<sub>2</sub>(010) || TiO<sub>2</sub>(011) || TiN(112) || Si(112). The inter-planar spacing of VO<sub>2</sub>(010) and TiO<sub>2</sub>(011) equal to 2.26 and 2.50 Å, respectively. This results in a 9.78% tensile misfit strain in VO<sub>2</sub>(010) lattice which relaxes through 9/10 alteration domains with a frequency factor of 0.5, according to the domain matching epitaxy paradigm. Also, the inter-planar spacing of VO<sub>2</sub>(011) and TiO<sub>2</sub>(011) equals to 3.19 and 2.50 Å, respectively. This results in a 27.6% compressive misfit strain in VO<sub>2</sub>(011) lattice which relaxes through 3/4 alteration domains with a frequency factor of 0.57. We studied semiconductor to metal transition characteristics of VO<sub>2</sub>/TiO<sub>2</sub>/TiN/Si heterostructures and established a correlation between intrinsic defects and magnetic properties.

### INTRODUCTION

Combination of semiconducting and magnetic properties has led to development of spintronic (spin based electronics). This achievement facilitates production of spin-based devices. Different materials have been investigated for this application and some semiconductors such as VO<sub>2</sub>, ZnO, TiO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, and In<sub>2</sub>O<sub>3</sub> have shown promising results at room temperature [1-5]. Among those VO<sub>2</sub> shows a strong correlated electron system with a small band gap (~0.7 eV at room temperature) but its magnetic properties have not been studied yet. VO<sub>2</sub> can serve as a smart material which generally responds to temperature, pressure variations and electric or magnetic fields. It is worth mentioning that VO<sub>2</sub> has semiconductor-to-metal transition (SMT) at about 340 K resulting from an ultrafast phase transformation from a high temperature tetragonal state to a low temperature monoclinic state [6-8].

Considering practical applications, there is a problem with the bulk VO<sub>2</sub> that it cannot withstand the repeated thermal cycling, while thin films and nanoparticles are more inclined to tolerate these stresses. Also, the SMT for films and nanoparticles can be tuned to room temperature, which makes their application very unique, such as, thermally activated optical switching [9,10], thermal relays and energy management devices [11,12], infrared sensors and actuators [13], micro-bolometers [14,15], electrochromic and photochromic memory and optical devices [16,17]. Magnetic, electrical, and optical properties of semiconductors are controlled through native defects. Also, they play a role in diffusion mechanism involved in growth, processing, and device degradation. Point defects affect electrical and optical properties of

semiconductors. These point defects consist of intrinsic native defects i.e. vacancies, interstitials, impurities, and defect complexes.

In this study, we provide a new platform of TiO<sub>2</sub>/TiN to grow bi-epitaxial VO<sub>2</sub> while integrated with Si(100). This paper focuses on the epitaxial relations across the interfaces. Metal to semiconductor transition for VO<sub>2</sub> are investigated and discussed. We report the magnetic properties of the VO<sub>2</sub> thin film and the role of defects in defining and tuning these properties is discussed.

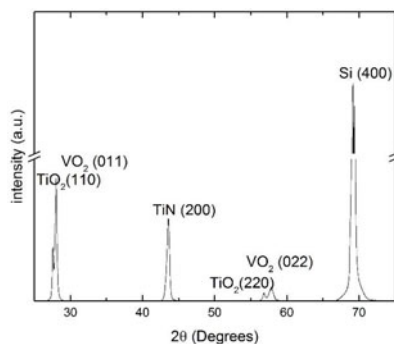
## EXPERIMENTAL DETAILS

The VO<sub>2</sub>/TiO<sub>2</sub>/TiN/Si thin film heterostructures were grown on Si(100) substrates employing pulsed laser deposition (PLD). A Lambda Physik (LPX200) KrF excimer laser, with  $\lambda=248$  nm,  $t=25$  ns, and the average power of 2.5 W was used to ablate the targets. The laser gas composition was 0.12% F<sub>2</sub>, 2.22% He, 4.6% Kr, and 92.94% Ne. The laser beam was incident at an angle of 45° on the surface of the targets which were rotated during the deposition to provide uniform ablation characteristics of the target surface. The energy density and repetition rate were set at 3-3.5 J.cm<sup>-2</sup> and 5 Hz. The TiN buffer was deposited at 920 K for 4000 pulses under 10<sup>-5</sup> Torr using a high density 99.9% pure TiN target. Through 2 min oxidation under oxygen pressure of 10<sup>-2</sup> Torr, half of TiN epilayer was oxidized to TiO<sub>2</sub> at 920 K [18]. The VO<sub>2</sub> layer was then deposited at 720 K under an oxygen pressure of 10<sup>-2</sup> Torr for 3000 pulses. The VO<sub>2</sub> target was made by sintering 99.5 % pure VO<sub>2</sub> powder under Ar atmosphere at 1100 °C for 12 h.

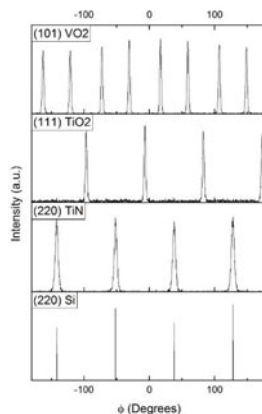
A Rigaku diffractometer with Cu-K $\alpha$  radiation ( $\lambda=0.154$  nm) was used to study the out-of-plane orientation of the films. A Philips X'Pert Pro diffractometer was employed for  $\phi$ -scan XRD to confirm in-plane alignment and epitaxial growth characteristics across the interfaces. Transmission Kikuchi Diffraction (TKD) mapping was carried out on FEI Quanta Focused Ion Beam. Sample was prepared by Focused Ion Beam (FIB), The FEI Quanta 3D FEG to be transparent to electron beam for TKD technique. The sample with pressed indium dots was mounted on a custom built rotatable pogo-pin setup in the PPMS. The magnetic measurements were done using Quantum design Super-conducting Quantum Interference Device (SQUID).

## DISCUSSION

Figure 1 shows the theta-2theta scan of X-Ray diffraction pattern of VO<sub>2</sub> thin film grown on the Si(100) substrate buffered with TiO<sub>2</sub>/TiN layers. The pattern represented either a highly textured or an epitaxial VO<sub>2</sub> layer with the out of plane orientation of (011). Thus, the out of plane relationship can be established as VO<sub>2</sub>(011)||TiO<sub>2</sub>(110)||TiN(100)||Si(100). In order to investigate the in-plane orientation relationship,  $\phi$  scan of X-Ray diffraction pattern (Figure 2) were performed on different reflection of the planes. The results reveal a cube-on-cube growth as for the TiN and Si crystals by DME paradigm. Four sharp  $\phi$ -signals from {111} family of planes of TiO<sub>2</sub> originate from (111) and ( $\bar{1}\bar{1}\bar{1}$ ) planes for (110)/( $\bar{1}\bar{1}\bar{0}$ ) as well as ( $\bar{1}\bar{1}\bar{1}$ ) and ( $\bar{1}\bar{1}\bar{1}$ ) planes for ( $\bar{1}\bar{1}\bar{0}$ )/( $\bar{1}\bar{1}\bar{0}$ ) of titania. The common direction between TiO<sub>2</sub>{110} and TiO<sub>2</sub>{111} planes is  $\langle\bar{1}\bar{1}0\rangle$  which has an azimuthal rotation of 45° with respect to TiN $\langle 100\rangle$  axis. The (101) reflection of VO<sub>2</sub> layer shows 8 peaks with intervals of 22.5° angular separation from each other. The common direction between VO<sub>2</sub>{101} and VO<sub>2</sub>{011} planes is  $\langle\bar{1}\bar{1}\bar{1}\rangle$  which has an azimuthal rotation of 22.5° with respect to Si $\langle 100\rangle$  and TiO<sub>2</sub> $\langle 110\rangle$  axis.

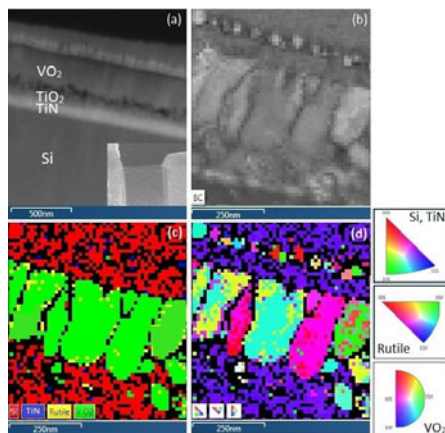


**Figure 1.** XRD  $\theta$ - $2\theta$  pattern acquired from the VO<sub>2</sub>(011)/TiO<sub>2</sub>(110)/TiN(100)/Si(100) heterostructure

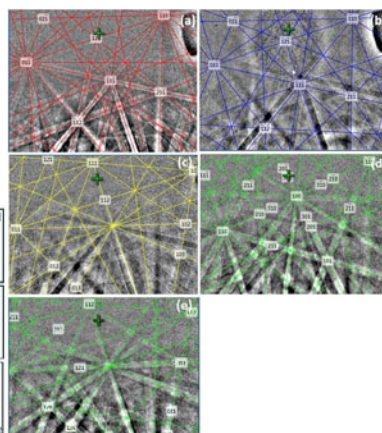


**Figure 2.** Results of XRD  $\phi$ -scan performed on the VO<sub>2</sub>(011)/TiO<sub>2</sub>(110)/TiN(100)/Si(100) heterostructure: Si(220) reflection, TiN(220) reflection, TiO<sub>2</sub>(111) reflection, and VO<sub>2</sub>(101) reflection

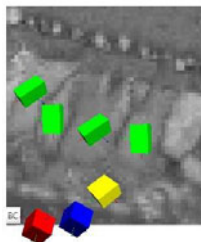
For additional details of alignment across interfaces, TKD data were collected from these heterostructures. Figure 3a represents the cross section electron image of the VO<sub>2</sub>(011)/TiO<sub>2</sub>(110)/TiN(100)/Si(100) heterostructures with the thickness of 110, 100, and 315 nm, for TiN, TiO<sub>2</sub>, and VO<sub>2</sub> layers respectively. The band contrast image is displayed in Figure 3b which shows where crystallographic direction has a major change. As it is clear in VO<sub>2</sub> layer there are vertical grain boundaries illustrating different directions. Figure 3c depicts VO<sub>2</sub>/TiO<sub>2</sub>/TiN/Si heterostructure's phase map and Figure 3d provides a pole figure map of layers. The Si and TiN have similar Kikuchi, also TiO<sub>2</sub> layer is so thin that makes it hard to detect with this technique. Inverse pole figure map also confirms there are two major colors in VO<sub>2</sub> layer suggesting two major orientations for observed grains. According to orientation map, two epitaxial relationships are established as VO<sub>2</sub>(010) and VO<sub>2</sub>(110)  $\parallel$  TiO<sub>2</sub>(011)  $\parallel$  TiN(112)  $\parallel$  Si(112). Figure 4 a, b, and c & d show the Kikuchi patterns of Si, TiN, TiO<sub>2</sub>, and two orientation of VO<sub>2</sub> respectively. These patterns also confirm the cube on cube alignment of Si and TiN. Also patterns of TiO<sub>2</sub> and VO<sub>2</sub> are in accordance with established relationship of VO<sub>2</sub>(110)  $\parallel$  TiO<sub>2</sub>(011) and VO<sub>2</sub>(010)  $\parallel$  TiO<sub>2</sub>(011). The orientations in VO<sub>2</sub> grains as represented in Figure 5 alternate between (010) and (110). The presence of two types of grains with different orientations explains the appearance of eight peaks in phi-scan XRD with four peaks belongs to each plane. The inter-planar spacing of VO<sub>2</sub>(010) and TiO<sub>2</sub>(011) equal to 2.26 and 2.50 Å, respectively. The mentioned matching results in a 9.78% tensile misfit strain in VO<sub>2</sub>(010) lattice which relaxes through 9/10 and 10/11 alteration domains with a frequency factor of 0.5, according to the domain matching epitaxy paradigm [19]. Also, the inter-planar spacing of VO<sub>2</sub>(011) and TiO<sub>2</sub>(011) equal to 3.19 and 2.50 Å, respectively. This results in a



**Figure 3.** TKD result of the FIB slice (a) Cross section electron image and the FIB made sample at the right corner, (b) Band contrast image, (c) Phase map image, and (d) Inverse pole figure map (IPF Y) of interfaces acquired from the  $\text{VO}_2(011)/\text{TiO}_2(110)/\text{TiN}(100)/\text{Si}(100)$  heterostructure



**Figure 4.** Kikuchi patterns of (a) Si, (b) TiN, (c)  $\text{TiO}_2$ , and (d, e)  $\text{VO}_2$  layers



**Figure 5.** Poles belong to each layer of Si, TiN,  $\text{TiO}_2$ , and  $\text{VO}_2$  in the cross section band contrast image, respectively from bottom to top

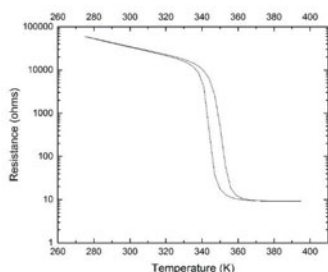
27.6% compressive misfit strain in  $\text{VO}_2(011)$  lattice which relaxes through  $2/3$  and  $3/4$  alteration domains with a frequency factor of 0.57.

Figure 6 displays the semiconductor to metal transition (SMT) temperature of  $\text{VO}_2/\text{TiO}_2/\text{TiN}/\text{Si}$  heterostructure. Sharp transition in the heterostructure was observed with amplitude of over 5 orders of magnitude. The hysteresis is about 8 K and transition temperature is 350 K.

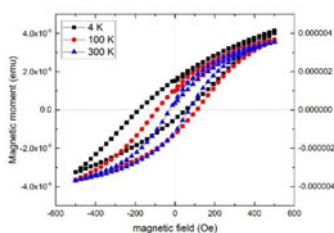
Magnetic properties of these films were measured by sweeping magnetic field from -600 to 600 Oe at three different temperatures of 4, 100, and 300 K. The hysteresis loops are shown in Figure 7. It is interesting to note the presence of ferromagnetism in VO<sub>2</sub> thin film. The presence of ferromagnetism is attributed to oxygen vacancy and reduction of Vanadium from V<sup>4+</sup> to V<sup>3+</sup>. In fact, the formation of oxygen vacancies is accompanied by the release of electrons to the lattice which is subsequently trapped by V<sup>4+</sup> cations to preserve charge neutrality. This phenomenon results in the formation of V<sup>3+</sup> cations. The formation of oxygen vacancies and V<sup>3+</sup> species can be explained by the following reaction:



Where V<sub>O</sub>'' represents an oxygen vacancy. This reaction stipulates that the non-stoichiometric VO<sub>2</sub> thin films have a higher charge carrier concentration (e<sup>-</sup>) and must exhibit a lower resistivity in the semiconducting state [7]. Ferromagnetic behavior in other heterostructure including VO<sub>2</sub> has been observed previously by our group [20].



**Figure 6.** Resistance versus temperature in VO<sub>2</sub>/TiO<sub>2</sub>/TiN/Si heterostructure



**Figure 7.** Magnetic field dependent magnetization of VO<sub>2</sub>(011) measurement at 4, 100, and 300 K with 200 Oe field cooling

## CONCLUSION

In this paper, we have successfully integrated VO<sub>2</sub> thin film on Si through buffer layer of TiO<sub>2</sub>/TiN. The TiN were grown cube-on-cube on Si, and TiO<sub>2</sub> was oxidized epitaxially with [110] out-of-plane orientation. VO<sub>2</sub> was then deposited on TiO<sub>2</sub> with out-of-plane direction

parallel to [011]. The in-plane relationship established to be  $\text{VO}_2(110)/\text{VO}_2(010) \parallel \text{TiO}_2(011) \parallel \text{TiN}(112) \parallel \text{Si}(112)$  based on transmission Kikuchi Diffraction. Metal to semiconductor transition was defined to be 350 K with 8 K hysteresis, according to resistance versus temperature hysteresis loop. We have observed the ferromagnetic behavior in  $\text{VO}_2$  samples and argued that it is due to the formation of oxygen vacancies or  $\text{V}^{3+}$  defects with unpaired electrons. Therefore, the formation of oxygen vacancies or non-stoichiometric oxidation state of vanadium in  $\text{VO}_2$ , is envisaged to be responsible for the observed room-temperature ferromagnetic characteristics.

## ACKNOWLEDGMENTS

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