Metal-insulator transition characteristics of VO₂ thin films grown on Ge(100) single crystals

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Phase transitions exhibited by correlated oxides could be of potential relevance to the emerging field of oxide electronics. We report on the synthesis of high-quality VO₂ thin films grown on single crystal Ge substrates by physical vapor deposition and their metal-insulator transition (MIT) properties. Thermally triggered MIT is demonstrated with nearly three orders of magnitude resistance change across the MIT with transition temperatures of 67°C (heating) and 61°C (cooling). Voltage-triggered hysteretic MIT is observed at room temperature at threshold voltage of \( \sim 2.1 \) V for \( \sim 100 \) nm thickness VO₂ films. Activation energies for electron transport in the insulating and conducting states are obtained from variable temperature resistance measurements. We further compare the properties of VO₂ thin films grown under identical conditions on Si(100) single crystals. The VO₂ thin films grown on Ge substrate show higher degree of crystallinity, slightly reduced compressive strain, larger resistance change across MIT compared to those grown on Si. Depth-dependent x-ray photoelectron spectroscopy measurements were performed to provide information on compositional variation trends in the two cases. These results suggest Ge could be a suitable substrate for further explorations of switching phenomena and devices for thin film functional oxides. © 2010 American Institute of Physics. [doi:10.1063/1.3492716]

I. INTRODUCTION

Vanadium dioxide (VO₂) undergoes a sharp metal-insulator transition (MIT) at \( \sim 340 \) K. Recently, it has been observed that the MIT in VO₂ can be triggered electrically in addition to the well-studied thermally induced MIT. Due to the near-room temperature transition and voltage-triggered MIT, a great deal of novel logic, memory, and sensor devices are being proposed utilizing VO₂. Particularly, the electrically triggered MIT in VO₂ is promising for potential applications as ultrafast switches, Mott field effect transistor, two-terminal memristive devices wherein one may use the phase transition-induced resistance change or nonlinear current-voltage (I-V) characteristics as a switch. A vertical device geometry is preferred among some of these novel VO₂ devices, particularly for using the phase transition element to control current flow in a device or circuit. To date, the most frequently used conducting substrate in vertical VO₂ devices is heavily doped Si. Comparing to the TiO₂ (Refs. 16 and 17) and sapphire substrates, the crystallinity of VO₂ thin films on Si substrate is compromised due to larger lattice mismatch and formation of interfacial oxides, however, TiO₂ and sapphire are insulating and may not be applicable as bottom contacts in VO₂ based out-of-plane devices. Heavily doped Ge substrates are conducting, and have a slightly smaller lattice mismatch with VO₂ than Si, but the VO₂ growth on Ge substrates has not been studied so far to the best of our knowledge. Further, Ge is a high mobility semiconductor that is attracting a great deal of interest in the transistor research community and hence is well-suited for this study. In this paper, we report on the synthesis of high-quality VO₂ thin films grown on Ge substrates with the observation of both thermally triggered MIT and room temperature voltage-triggered MIT. To the best of our knowledge, this is the first report on growth and functional properties of VO₂ films on single crystal Ge.

II. EXPERIMENTS

VO₂ thin films were grown on heavily doped n⁺-Ge (100) single-crystalline substrates (\( \sim 0.008 \) \( \Omega \) cm resistivity) and reference n⁺-Si (100) single-crystalline substrates (0.002–0.005 \( \Omega \) cm resistivity) simultaneously with identical growth conditions using radio frequency (rf) sputtering technique with a V₂O₅ target. Numerous growth experiments were carried out to identify optimal growth conditions for good quality films. The VO₂ thin film growth is quite sensitive to the oxygen gas flow rate. Figure 1 shows an example of flow rate effect on VO₂ thin films grown on sapphire substrates using V₂O₅ target at growth temperature and pressure of 550 °C and 5.0 mTorr. The total Ar and O₂ gas flow rate is 100 SCCM (SCCM denotes cubic centimeter per minute at STP). Figures 1(a)–1(d) show the resistance ratio between 25 and 100 °C for VO₂ thin films of 413 nm thickness on (green), 968 (blue), 1051 (red), and 14 (black) for O₂ gas flow rates of 0 SCCM, 0.5 SCCM, 0.8 SCCM, and 1.0 SCCM, respectively. The O₂ gas flow rates and resistance ratios are summarized in Fig. 1(e). The sensitivity of VO₂ properties on synthesis conditions has been noted in earlier studies as well and this is due to the fact that vanadium can readily exist in multiple valence states leading to several Mott-Nielseni phases. Hence, great care is needed in determining optimal growth conditions that include control over the oxygen pressure during growth to obtain VO₂ films with...
such as H2O851 respectively. The grown on Ge and Si substrates as red and green curves, re-
both the VO2 thin films on Ge and Si substrates is estimated to be +4% lattice constant mismatch.19 Hence, it is reasonable that the growth direction of both VO2 thin films are along the same orientation [011], indicated by the XRD patterns. Several minor orientations appear in the XRD pattern of VO2-on-Si but not VO2-on-Ge, such as [200], [002], and [210], indicating qualitatively that the VO2-on-Si is less textured than VO2-on-Ge. Figure 2(b) shows the Gaussian fits (blue solid lines) to the (011) XRD peaks of VO2-on-Ge (red symbols) and VO2-on-Si (green symbols). The full-width-at-half-maximum (FWHM) of the (011) XRD peaks of VO2-on-Ge and VO2-on-Si is 0.50° and 0.70°, respectively.

III. RESULTS AND DISCUSSION

Figure 2(a) shows XRD patterns of VO2 thin films grown on Ge and Si substrates as red and green curves, respectively. The (011) peak dominates in the XRD patterns of both the VO2 thin films on Ge (VO2-on-Ge) and the VO2 thin films on Si (VO2-on-Si). Si and Ge possess the same crystal structure of diamond but an ~4% lattice constant mismatch.19 Hence, it is reasonable that the growth direction of both VO2 thin films are along the same orientation [011], indicated by the XRD patterns. Several minor orientations appear in the XRD pattern of VO2-on-Si but not VO2-on-Ge, such as [200], [002], and [210], indicating qualitatively that the VO2-on-Si is less textured than VO2-on-Ge. Figure 2(b) shows the Gaussian fits (blue solid lines) to the (011) XRD peaks of VO2-on-Ge (red symbols) and VO2-on-Si (green symbols). The full-width-at-half-maximum (FWHM) of the (011) XRD peaks of VO2-on-Ge and VO2-on-Si is 0.50° and 0.70°, respectively.

Figure 2(a) shows XRD patterns of VO2 thin films grown on Ge (red) and Si (green) substrates. (b) Gaussian fits (blue solid lines) of (011) XRD peaks of VO2-on-Ge (red symbols) and VO2-on-Si (green symbols). The FWHM of the (011) XRD peaks of VO2-on-Ge and VO2-on-Si is 0.50° and 0.70°, respectively.

The plot of resistance in VO2 thin films with O2 gas flow rate of 0, 0.5, 1.0, and 2.0 SCCM using V2O5 target at 550 °C and 5.0 mTorr. The total Ar and O2 gas flow rate is 100 SCCM. (e) The plot of resistance ratio between 25 and 100 °C of the VO2 thin films as a function of O2 gas flow rate.

FIG. 1. (Color online) [(a)–(d)] The temperature dependence of normalized resistance in VO2 thin films with O2 gas flow rate of 0 (green), 0.5 (blue), 1.0 (red), and 2.0 (black) SCCM using V2O5 target at 550 °C and 5.0 mTorr. The total Ar and O2 gas flow rate is 100 SCCM. (e) The plot of resistance ratio between 25 and 100 °C of the VO2 thin films as a function of O2 gas flow rate.
the existence of a slight mixture valence of vanadium in the film, which is very close to the +2 V valence position (V $2p_{3/2}$ at 513.7 ± 0.2 eV for +2 valence)\textsuperscript{24–31} In the VO$_2$-on-Ge, this shoulder peak persists until the interface between VO$_2$ and Ge [Fig. 3(b)], however, the shoulder peak eventually dominates and becomes a separate peak near the interface between VO$_2$ and Si [Fig. 4(b)], representing a lower valence state of vanadium. This indicates that the VO$_2$-on-Si shows a more evident off-stoichiometry than VO$_2$-on-Ge near the interface region. Figure 5(a) shows an example of how the relative fraction of each valence state of vanadium is extracted from the fitting analyses. The V $2p_{3/2}$ XPS peak (in the high-resolution XPS spectra) was deconvoluted to two V $2p_{3/2}$ peaks with +4 and +2 valences. The ratio of the areas underneath the two deconvoluted peaks (after subtraction of the Shirley baseline background) gives the relative fraction of the mixture. Figure 5(b) shows detailed analyses results of the relative fraction of +4 valence vanadium in the VO$_2$-on-Ge (red) and VO$_2$-on-Si (green). The VO$_2$-on-Ge shows a high fraction of +4 near the surface (>80%). Both VO$_2$-on-Ge and VO$_2$-on-Si show good stoichiometry (~70%) in center region of the films (~10 nm below the surface and ~20 nm above the interface), while the VO$_2$-on-Ge shows a slightly higher fraction of +4 valence. When the VO$_2$ thin films reach the near-interface regions, the fraction of +4 valence in the VO$_2$-on-Si decreases much faster than that of the VO$_2$-on-Ge. This could potentially arise from interfacial reaction with the silicon substrate owing to its propensity to form silicon oxides while germanium oxide is less stable from thermodynamic considerations.\textsuperscript{34,35} The error bars in Fig. 5(b) arise from the fitting uncertainties of the inaccuracy. As noted earlier, stoichiometry control is particularly difficult for VO$_2$ growth due to presence of Magnéli phases\textsuperscript{32} in this system and ease of vanadium to take on several possible oxidation states. Slight off-stoichiometry with mixture of several valence states of vanadium is common, especially when the Si or glass substrates are used instead of TiO$_2$ or sapphire substrates.\textsuperscript{24–31} Our results are consistent with these prior reports and a slight degradation in resistance ratio across the MIT is to be expected when compared to single-crystalline films on lattice-matched insulating substrates or bulk single crystals.

Figure 6(a) shows the temperature dependence of the normalized in-plane resistance [$R(T)/R(20\,^\circ C)$] of the VO$_2$-on-Ge substrate (red circles) and VO$_2$-on-Si (green circles). The resistance of the VO$_2$ thin film at each temperature point is determined by the reciprocal slope of an in-plane linear I-V scan between two probes. (The linear I-V curves indicate Ohmic contacts\textsuperscript{36} between the probes and the VO$_2$ thin film.) The solid and open circles represent temperature ramping up and down, respectively. Nearly three orders of magnitude resistance change is observed from 20 to 100 °C in the VO$_2$-on-Ge, but less than two orders change in VO$_2$-on-Si, indicating a higher quality VO$_2$-on-Ge than VO$_2$-on-Si, consistent with the XPS and XRD results. Using Gaussian fittings on the derivative logarithmic plot of
respectively, using Gaussian fits on the derivative logarithmic plots. 67.3 °C and 60.8 °C during temperature ramping up and ramping down, respectively. The MIT temperature is estimated.

The MIT temperature of the VO2-on-Ge is determined to be 67.3 °C and 60.8 °C during temperature ramping up and ramping down, respectively, as shown in Fig. 6(b), while 67.3 °C and 58.6 °C for VO2-on-Si during temperature ramping up and ramping down, respectively, as shown in Fig. 6(c). The VO2-on-Ge shows 2.2 °C narrower MIT width (6.5 °C versus 8.7 °C) than the VO2 thin film on Si. The minor difference in the transition temperature and MIT width between VO2-on-Ge and VO2-on-Si is possibly due to variation in the faction of +4 valence [other valence vanadium oxide phases can distort the MIT (Ref. 31)] and strain within the films as discussed earlier. However, the observed thermal-MIT hysteresis window width and transition temperatures in both VO2 thin films show consistent trends with previous reported values.

Figure 7(a) shows the plot of logarithmic resistance versus reciprocal temperature (1/T), which is employed for the activation energy (Ea) analyses. The activation energy is estimated by the slope of a linear fitting of Ln(R) over (1/kT), as Ln(R) = b + Ea/kT, where R, T, k, and b are resistance, temperature (in unit K), Boltzmann constant, and intercept. Figures 7(b) and 7(c) show the activation energy of VO2-on-Ge (red) and VO2-on-Si (green) in low-temperature “insulating” and high-temperature “metallic” states. The activation energy of VO2-on-Ge is 193 ± 7 meV and 149 ± 4 meV for low- and high-temperature states, respectively. The reason that the high-temperature activation energy is not significantly smaller than that of the low-temperature is likely due to the mixed valence states of the VO2 thin films. Once the temperature ramps up across the MIT transition temperature, only the VO2 phase in the film undergoes transition into the metallic state. In other words, even at high temperatures the film is not entirely metallic;
hence the activation energy is not significantly smaller than its low-temperature insulating state. In a previous study, for example, a VO$_2$ thin film with nearly four orders of magnitude resistance change in thermal-MIT, which is closer to the ideal VO$_2$, shows a smaller high-temperature activation energy than the low-temperature one (80–90 meV versus 230–250 meV). For the VO$_2$-on-Si sample, again due to mixture of valences and smaller order of resistance change across MIT than VO$_2$-on-Ge, the high-temperature activation energy is not distinct from the low-temperature one, considering the error bars. This likely indicates that the high-temperature state is a mixture of metallic VO$_2$ regions and some insulating phases (from other valence vanadium oxide phases). Similar results on uniform temperature dependence of resistance on both sides of the MIT were also observed previously in off-stoichiometric VO$_2$ films grown by electron-beam evaporation. We do note here that the estimated activation energies are comparable to previous studies, prepared VO$_2$ using powder sintering method and found an activation energy of 240 meV from temperature dependence of the electrical conductivity analyses. Sahana et al. grew VO$_2$ thin films on glass substrates by chemical vapor deposition and the temperature-dependent resistance measurements indicated that the activation energy of the VO$_2$ thin films ranged from 180–260 meV depending on growth conditions.

Figure 8(a) shows the I-V characteristics of VO$_2$-on-Ge measured in vertical geometry between 0 and 5 V at 25 °C (red), 60 °C (green), and 90 °C (blue). Voltage-triggered MIT is observed at 25 °C with threshold voltage at ~2.1 V. The inset in Fig. 8(a) shows the magnified region of the resistive hysteresis window of the I-V curves at 25 °C, with scan directions marked with arrows. The width of the voltage triggered MIT window is ~1 V. Considering the ~100 nm thickness of the VO$_2$ thin film, the threshold electric-field for triggering MIT is approximately $2.1 \times 10^7$ V/m at 25 °C, also in good agreement with studies on both VO$_2$ planar junctions on sapphire and capacitor-type devices on silicon. In the hysteresis curves, some “staircase” discontinuity shapes are observed, which is likely due to grain boundary or domain related contributions to MIT. Similar phenomena were also observed in nanoscale VO$_2$ planar junctions by Sharoni et al., who concluded that the thermal-MIT in VO$_2$ occurs through a series of staircase shape avalanches induced by impact ionization due to grain boundary effects. The effects were seen primarily in nanoscale junctions and hence reasonable to expect in our measurements since we are studying voltage-triggered phase transition across an ~100 nm film. Each staircase step may correspond to a grain/domain boundary associated change (slight differences in the insulating state conductivity lead to shifts in the critical voltage needed to initiate the transition and hence a step-like shape emerges). Electrically triggering MIT studies by conducting atomic force microscopy but in regions smaller than a single grain size, shows free of staircase steps in the I-V curves, which supports the analyses here and those in Ref. 45.

Figure 8(b) shows the Poole–Frenkel (PF) plot [Ln(I/V) versus Sqrt (V)] of the I-V curves shown in Fig. 8(a). At large voltages (> ~3.1 V), the VO$_2$ thin film shows metallic behavior over a broad range of temperature. At low voltages (< ~0.7 V), the VO$_2$ thin film only shows metallic behavior at high temperatures, but behaves as insulator at lower temperatures. At intermediate bias voltages and below thermal-MIT temperature, the PF mechanism dominates the conduction, indicated by the linear dependence of Ln(I/V) over Sqrt (V). The two bold blue lines in the PF region is for visual guidance, indicating the dominating of PF conduction mechanism in that region.

IV. SUMMARY

VO$_2$ thin films were grown on Ge(100) single crystal substrates using rf sputtering. Thermally triggered MIT with nearly three orders of magnitude resistance change with an
MIT width of ~6 °C is observed in VO₂ thin films grown on Ge. Hysteretic voltage-triggered MIT is observed at room temperature at a critical voltage of ~2.1 V with a hysteresis window of ~1 V in VO₂ thin films grown on Ge. The structural and electrical measurements suggest that Ge may be a suitable substrate for further explorations of phase transition-based oxide electronics utilizing MITs.

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19In monoclinic VO₂, lattice constant a=0.5753 nm. The lattice constants of Si and Ge are 0.5431 nm and 0.5646 nm, respectively.
33A. Patterson, Phys. Rev. 56, 978 (1939).