Nanostructure and thermal-optical properties of vanadium dioxide thin films

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A novel nanopolycrystalline structure of vanadium dioxide thin films is deposited on silicon or fused silica substrates by reactive ion sputtering and followed by an annealing. The characteristic analysis shows that the films have a columnar nanostructure with an average grain of 8 nm. The resistivities as a function of ambient temperatures tested by four-point probes for as-deposited films present that the transition temperature for nanostructure of vanadium dioxide films is near 35 °C which lowers about 33 °C in comparison with the transition temperature at 68 °C in its microstructure.

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The vanadium dioxide (VO_2) thin film materials are of special interest both for scientific investigation and for use in various technological applications because its transition temperature near 68 °C is the nearest room temperature among all semiconductor-to-metal phase transition materials and because its optical properties change appreciably in visible and infrared ranges of the spectrum during this transition. The potential applications include optical switch devices[1,2], uncooled infrared sensors[3−5], optical modulators[6], smart windows for solar energy utilization etc.[7,8]. For smart window application the VO_2 thin films exhibit infrared transparent at $T < T_c$, however it becomes infrared reflection for wavelength more than 1 μm at $T > T_c$. Where T_c is the phase transition temperature, and T is the ambient temperature. It is evident that the transmittance of infrared solar radiation, which carries total solar energy of about 50%, is diminished as the ambient temperature becomes more than the transition temperature in VO_2 thin films, indicating a possibility to develop energy-effect window coatings. People can lower electricity bill by 30% via using the smart windows in summer time alone and can also save fuels if used for automobiles[7−9]. For uncooled infrared sensor application the temperature coefficient of resistance ($\mathrm{TCR} = R^{-1}\mathrm{d}R/\mathrm{d}T$) is currently 2% $°\mathrm{C}^{-1}$ which is operated in semiconductor region of VO_2. A possibility of developing a high sensitivity VO_2-based microbolometer operating in the hysteretic region with a abrupt TCR of about 200% $°\mathrm{C}^{-1}$ has been proposed[10,11], which would approach the sensitivity based on cooled infrared sensors such as mercury cadmium telluride (MCT) detectors and would drop down the price by two orders of magnitude. For the two kinds of applications mentioned above, a preferable transition temperature of VO_2 films should be near room temperature, e.g. 30 °C[8,11].

The VO_2 has been fabricated using an ion beam sputtering system. A vanadium target with ϕ4 inch and purity of 99.8%, and a mixture gases of Ar (99.998%) and O_2 (99.998%) are used for the deposition. Silicon and fused silica are used as substrates. VO_2 films deposited by reactive ion sputtering are completed at temperature of 300 °C and followed by a post-annealing at temperatures between 460—480 °C for 40 minutes.

The nanocrystalline structure of VO_2 films has been characterized by a bright-field high-resolution transmission electron microscope (HRTEM) with model of JEOL2010FEF made in Japan. Figure 1 shows the columnar nanostructure of as-deposited VO_2 films. A buffer layer of Si_3N_4 is deposited on silicon (001) substrate (the substrate not shown) and the nanocrystallites of VO_2 with an average size of 8 nm are grown on the Si_3N_4 buffer layer. Figure 2 shows a high-resolution electron diffraction pattern for nanocrystalline VO_2. In general, a single crystal in high-resolution electron diffraction pattern has a periodic diffraction dot array, and a poly-crystal has diffractive rings with sharp diffraction lines, however an amorphous phase has broad featureless halos due to lack of crystalline structure. The film shown in Fig. 2 indicates a mixture of polycrystalline and amorphous VO_2 structure. The surface morphology of VO_2 film obtained

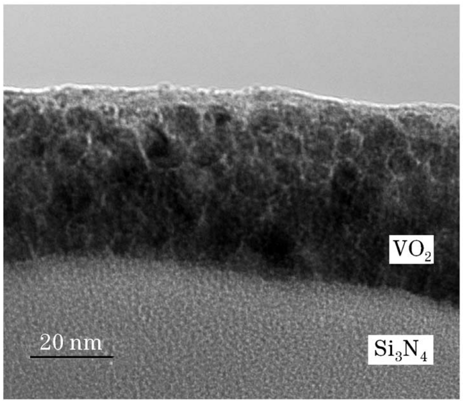

Fig. 1. Schematic cross-section of a bright-field high-resolution transmission electron microscope for a VO_2 nanostructure film. The nanocrystalline VO_2 is deposited on amorphous silicon nitride (silicon substrate not shown, and a fused silica substrate instead of silicon is available).

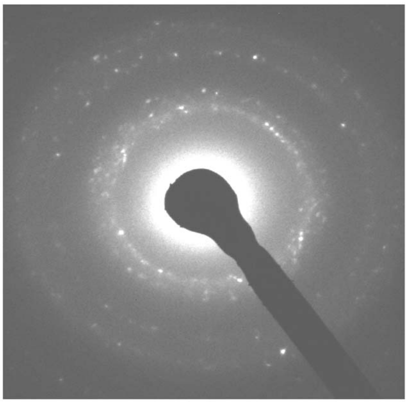

Fig. 2. High-resolution electron diffraction pattern for VO_2 nanocrystalline film.

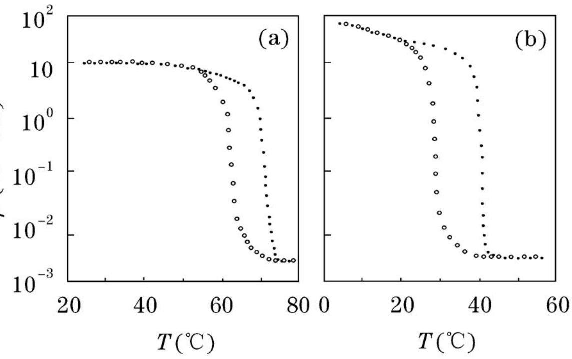

Fig. 3. The change of resistivities of VO_2 thin films with the ambient temperature (the hysteresis for microstructure with crystallites of 1—2 μm (a) and for nanostructure with an average size of about 8 nm (b)). Dots present heating curve and circles present cooling curve.

by scanning electron microscope is very smooth and homogeneous, and the crystallites are very fine and compact.

The resistivities as a function of ambient temperature in a VO_2 film have been completed by using four-point probe measurement. The temperature change is provided using a semiconductor temperature controller and the temperature is measured at the same time by pressing a thermocouple against the film surface. Figure 3 shows the change of resistivities of VO_2 thin films with ambient temperature. The transition temperature in nanostructure of VO_2 lowers 33 °C in comparison with that of microstructure. It is known that transition temperature of VO_2 material can also be decreased by doping tungsten or other elements, such as Nb, Mo, F and Ta in proper amount[12]. To make sure if there are any impurities as doping in the film during the deposition processes, we can not find any impurities in all experimental samples except for carbon. Figure 4 shows the spectrum by surface X-ray photoelectron spectroscopy (XPS) with binding energy up to 1000 eV. The nanocrystalline VO_2 thin films for the XPS analysis have been deposited on silicon substrate with a buffer layer of Si_3N_4. The XPS results indicate that there are only three elements: carbon, vanadium, and oxygen, in the spectrum where carbon peak is from the surface contamination of VO_2 films. Transmittance spectra of VO_2 before and after the phase transition have been measured. Figure 5 shows optical transmittance of VO_2nanocrystalline film on silica substrate. It can be found that the optical contrast is improved in comparing with the VO_2 film in microstructure.

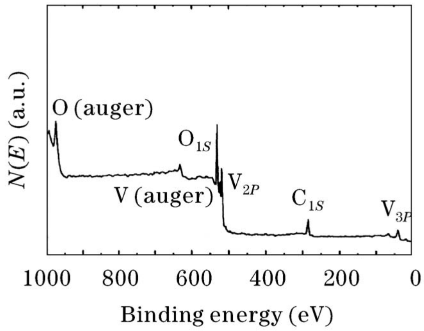

Fig. 4. Surface analysis of X-ray photoelectron spectroscopy.

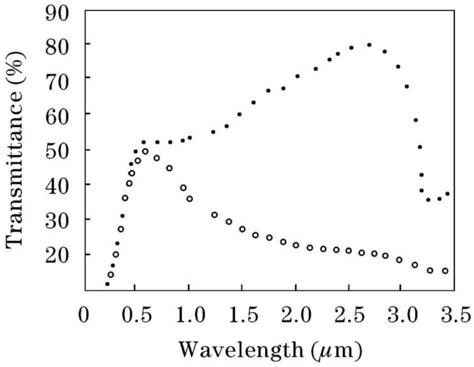

Fig. 5. Optical transmittance of VO_2 nanocrystalline film on silica substrate at 20 °C (dots) and 45 °C (circles). The thickness of VO_2 film is 80 nm.

The relative resistivity contrast (resistivity ratio before and after phase transition) can be controlled by modulating oxidation proportion (x of VO_x) in nanocrysatlline VO_2 films and by changing process parameters of both deposition and annealing. The properties of the VO_2 film can be controlled by adjusting the sputtering parameters of oxygen gas ratio, temperature and biasing of the substrate, and the ion bombardment. The stoichiometry of the sputtered VO_2 film is extremely sensitive to the oxygen fraction in the supporting ambient. The nanostructure of VO_2 films is strongly influenced by the substrate temperature. The high substrate temperature can produce the films with large grain size. Obvious change of the grain size with the increase of the oxidation time is not observed. It is very critical to control the substrate temperature to obtain nanostructure VO_2 thin films. It can be adjusted between 2 and 5 orders of magnitude, and the changes of resistivity contrast in the nanostructure are greater than that in the microcrystalline structure. An investigation for the optical properties in nanostructure VO_2 films is in progress. We believe that these original findings of VO_2 films nanostructure and relative properties will play an important role to extend relative potential applications.

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