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# THE FINITE SIZE EFFECT ON THE METAL-INSULATOR TRANSITION OF MOCVD GROWN $VO_2$ FILMS*

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# THE FINITE SIZE EFFECT ON THE METAL-INSULATOR TRANSITION OF $VO_2$ FILMS GROWN BY MOCVD

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ABSTRACT

We studied the finite size effect on the metal-insulator phase transition and the accompanying tetragonal to monoclinic structural phase transition of $VO_2$ films grown by MOCVD. X-ray diffraction measurements and electrical conductivity measurements were done as a function of temperature for $VO_2$ films with out-of plane particle size ranging from 60-310Å. Each $VO_2$ film was grown on a thin $TiO_2$ buffer layer, which in turn was grown by MOCVD on a polished sapphire (1120) substrate. The transition was found to be first order. As the out-of plane particle size becomes larger, the transition temperature shifts and the transition width narrows. For the 60Å film the transition was observed at ~61°C with a transition width of ~10°C, while for the 310Å film the transition temperature was ~59°C and the transition width ~2°C. We also observed thermal hysteresis for each film, which became smaller with increasing particle size.

## INTRODUCTION

The metal-insulator phase transition (MIPT) is a subject of intense theoretical[1] and experimental[2-6] interest. In spite of the similarities in the structural and electronic properties of metal oxide systems the nature of the MIPT can be first order in some systems such as $VO_2$[1,2] or continuous in others such as $NbO_2$[3].

MIPT for bulk system occurs at ~67°C and is accompanied by a slight structural distortion from a tetragonal rutile structure in the high temperature metallic phase to a monoclinic structure in the low temperature insulating phase[2,4].

In this paper we present the result of simultaneous x-ray diffraction and electrical conductivity measurements of MIPT for $VO_2$ films grown by MOCVD as a function of the out-of plane particle size (d(Å)) of the film. We observed thermal hysteresis for each film which is consistent with the first order nature of the transition. Also, as the out-of plane particle size increases, the transition temperature shifts and the transition width becomes narrower. We attempt to compare this result with the finite size effect on the first-order transition[7].

## EXPERIMENTAL

The detailed description of our deposition system and sample preparation procedure was presented elsewhere[5,8,9].

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The $VO_2$ films were grown on a uniformly thin (~125Å) $TiO_2$ buffer layer which in turn was grown using MOCVD on a polished sapphire (1120) substrate. By growing the $VO_2$ at 500°C on $TiO_2$ we could obtain good quality epitaxial films of monoclinic structure with in-plane particle size of ~1000Å at room temperature[5,8,9]. The $VO_2$ growth plane was (200) which is, in effect, the tetragonal rutile (101) plane.

The (313) diffraction peak was used to determine the particle size of $VO_2$ films and to study the structural transition. It was chosen because odd integer reflections are directly related to the order parameter[4], there are no reflections nearby from the $TiO_2$ buffer layer, and there is no contribution of a higher harmonic ($\lambda/2$) originated from graphite monochromator (0004) and sapphire substrate (1120) reflections.

The temperature was regulated within 1°C fluctuation during measurement.

## RESULTS and DISCUSSIONS

The effect of small crystallite size is manifested by the width of the x-ray diffraction peaks. The peak width can be expressed in terms of the crystallite size in the size range up to ~1000Å (x-ray coherence length). The particle size of the film can be obtained by $L=1.88\pi/\Delta q$, where $\Delta q$ is the FWHM of the diffraction peak in terms of longitudinal momentum transfer, and is corrected for instrumental broadening[10].

Since $VO_2$ grows with the (200) growth plane on $TiO_2$, we can determine the out-of plane particle size of films with h scans. From the scans of $VO_2$ (313), as shown in Fig 1, the out-of plane particle size of films we used were determined to be of 60, 120, 155, 170, 215 and 310Å.

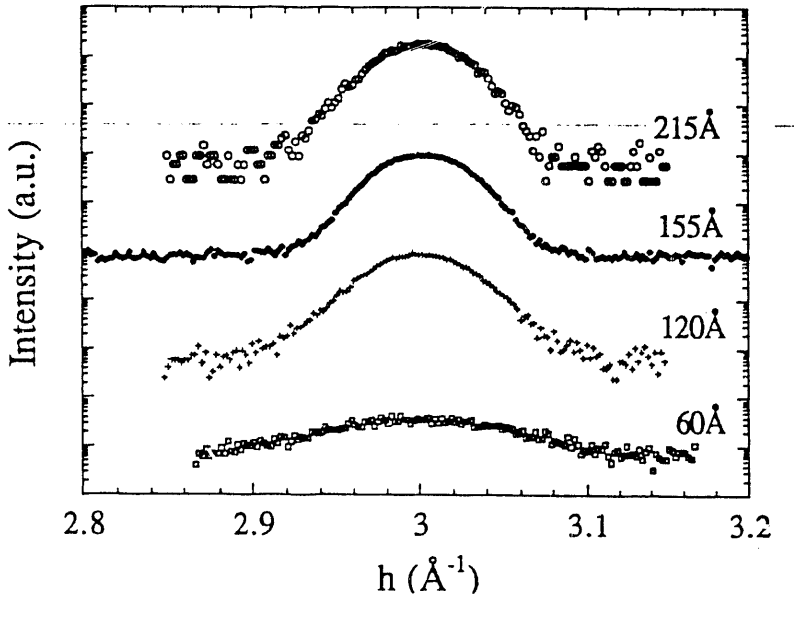


Fig 1 The h scans of (313) plane. For display purpose, we show 4 out of 6 scans, and scans were offset for clarity.

Fig 2(a) shows the temperature dependent behavior of the integrated intensity of (313) diffraction peak for the 310Å thick film in the vicinity of the phase transition for both heating and cooling. The transition temperature appears to be ~60°C and ~58°C for heating and cooling, respectively. Thermal hysteresis was observed for all samples, which becomes larger for the thinner films.

The temperature dependent electrical conductivity during heating for films with different particle size are shown in Fig 2(b). Here, the conductivity values were normalized by the room temperature (27°C) value for each film. As shown in the insert of Fig 2(b), we observed thermal hysteresis between 2 and 10K at the MIPT. The thermal hysteresis observed in the electrical conductivity is consistent with that observed in the x-ray diffraction measurement.

Near the transition temperature, only the total number of free (or conduction) electrons, n, created by the MIPT, determines the electrical conductivity ($\sigma \propto n$) if we assume that other parameters (phonon-electron scattering etc.) remain nearly constant. Then the entropy of electrons contributing to the electrical conductivity, S, is proportional to $ln\ n \propto ln\ \sigma$. If we denote the entropy during cooling and heating as $S_{up}$ and $S_{down}$, the energy fluctuation, $<|\Delta E|>$, in the transition region is proportional to $T(S_{down}-S_{up}) \propto T(ln\sigma_{down}-ln\sigma_{up})$. Then, heat capacity is proportional to $<|\Delta E|^2>/T^2 \propto [ln(\sigma_{down}/\sigma_{up})]^2$. Fig 3(a) shows $[ln\ (\sigma_{down}/\sigma_{up})]^2$ as a function of temperature for films 310Å, 120Å and 60Å thick.

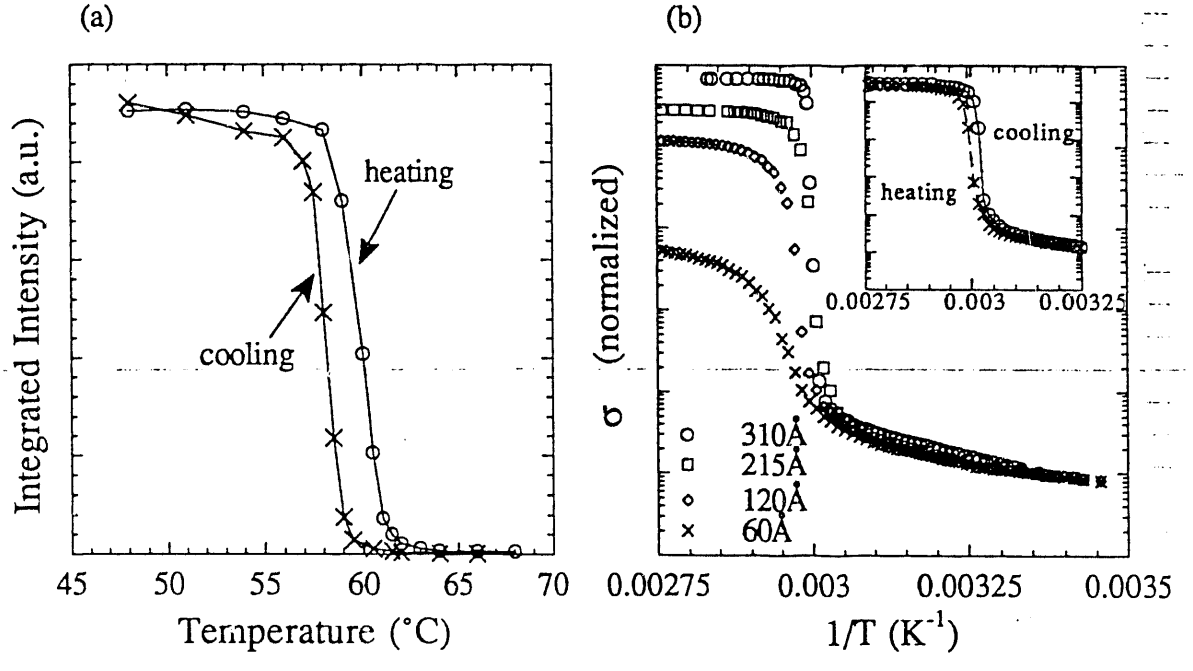


Fig 2(a) Temperature dependence of the integrated intensity of x-ray diffraction of (313) plane for the $VO_2$ film with out-of plane particle size of 310Å.

(b) Temperature dependent electrical conductivity of $VO_2$ films of various particle size during heating. Insert shows thermal hysteresis for the $VO_2$ film with out-of plane particle size of films of 215Å .

We define the transition temperature, $T_c$, from peak position and transition width, $\Delta T_w$, from FWHM of the specific heat.

One of the important observation is, as shown in Fig 3, that the smaller the particle size of the $VO_2$ film, the larger transition width. This phenomena is believed to be due to the finite size effect. The temperature-driven first-order phase transition shows a $\delta$-function-like singularity in the heat capacity at the transition temperature for infinitely large system. However, it is known that this transition becomes rounded and shifted for a finite size system[7]. For the first order transition, it is predicted that the rounding and shifting are inversely proportional to the particle sizes. In other words, the transition width and the shift in the transition temperature between infinite and finite sizes are linearly dependent on 1/d(Å) for our sample.

In our case, the conductivity of the $VO_2$ films is only dependent on the out-of plane particle size of films, because the in-plane dimensions of the film are large enough to ignore the finite size effects. $T_c$ and $\Delta T_w$ for each film as a function of the inverse particle size of film are shown in Fig 3(b). As predicted[8], we clearly see the finite size effect in that the transition width linearly approaches zero, as the particle size becomes larger.

Consistent with the theory on the finite size effect of the first-order transition[7], the transition temperature of MIPT for the $VO_2$ films linearly decreases to a certain value, ~58°C, with increasing out-of plane particle size of films up to 200Å. However, $T_c$ appears to deviate and shift to higher temperature from linear dependence for particle sizes than 200Å. The reason is not clear at this stage. However, one possibility is that the film, at least up to 200Å, may be influenced by the substrate and

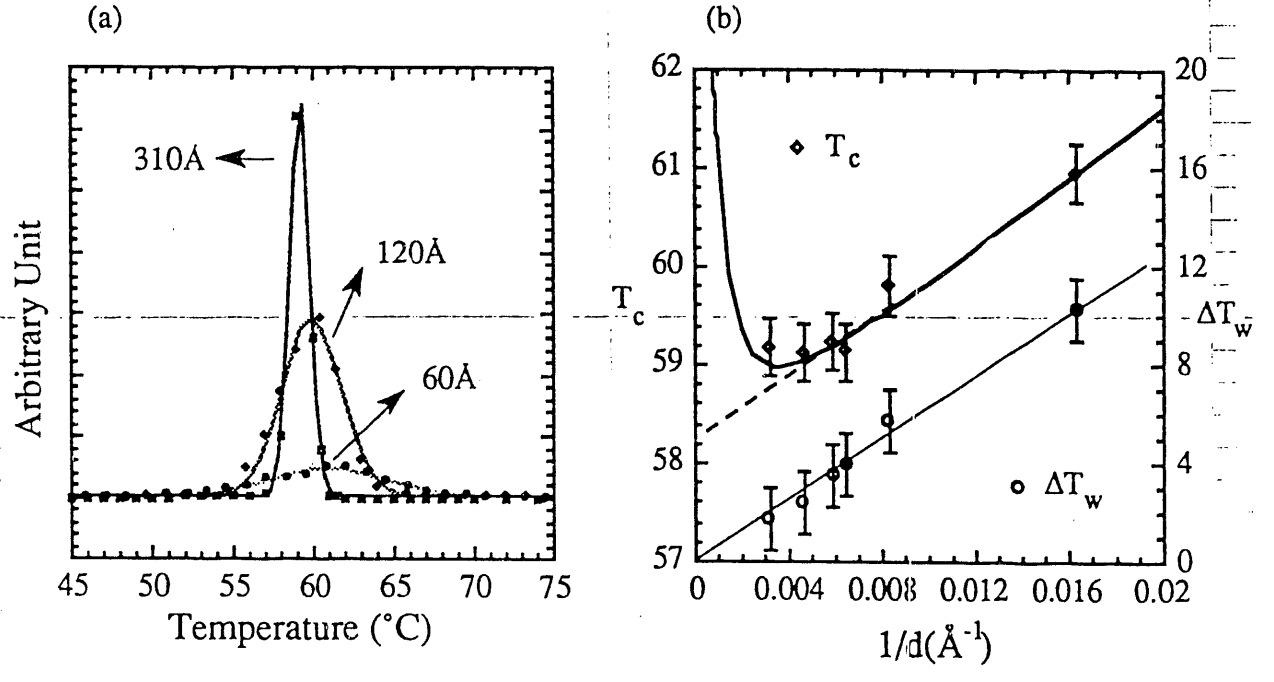


Fig 3(a) Calculated heat capacity from electrical conductivity.
(b) Transition temperature $T_c$ and transition width $\Delta T_w$ of metal insulator transition in $VO_2$ film as a function of 1/out-of plane particle size.

therefore $T_c$ is suppressed to a lower temperature[11]. As the film becomes thicker and therefore the substrate interaction is not important, the transition temperature will then sharply turn to that of bulk.

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