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Effect of W doping in metal–insulator transition material VO_2 by tunnelling spectroscopy

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Abstract

We used tunnelling spectroscopy to study heavily W doped VO_2 crystal in the temperature region across the phase transition. A double pseudo-energy-gap structure was observed across the Fermi level at temperatures below the phase transition. When the temperature was increased across the phase transition, the outer gap structure disappeared and an inner gap structure of about 0.4 eV became sharp. The tunnelling results explained the qualitative changes in the heavily doped sample from lightly doped one in the behaviour of the temperature dependence of electrical resistivity near the metal–insulator transition.

1. Introduction

The temperature-dependent phase transition in vanadium dioxide (VO_2), first observed by Morin in 1959, has attracted interest as a result of its possible useful applications, e.g. in temperature sensing devices, optical switching devices etc, because of the dramatic changes in electrical resistivity and infrared transmission [1–3]. It is well known that this phase transition, the so-called metal–insulator transition (MIT), is accompanied by a structural change from a high-temperature rutile type to a low-temperature monoclinic type [4]. Therefore, although this MIT is widely regarded as a Mott–Hubbard transition, the role of the Peierls distortion of the crystal structure in the low-temperature phase has been a topic of intense debate.

In order to use VO_2 in the above-mentioned applications, it is necessary to tailor the MIT temperature (T_t). Generally, the doping effect is one of the most promising methods for controlling T_t in phase transition materials. Doping metal ions into the VO_2 has also been shown to increase or decrease the T_t depending on factors such as the size and charge of the dopant ion in the VO_2 [5]. For example, T_t is lowered by doping metal elements such as W and Mo. In contrast, some elements such as Cr and Fe have been reported to raise T_t. In this paper,

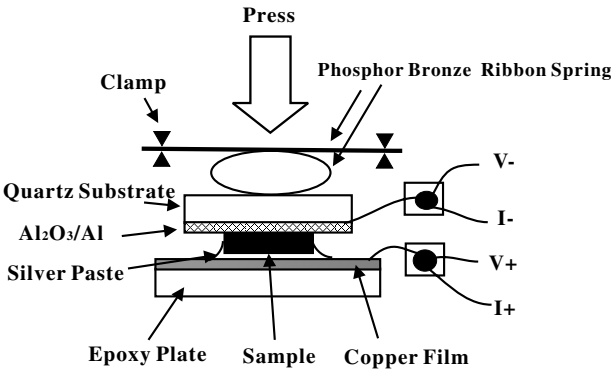

Figure 1. Schematic planar contact tunnel junction employed in this study.

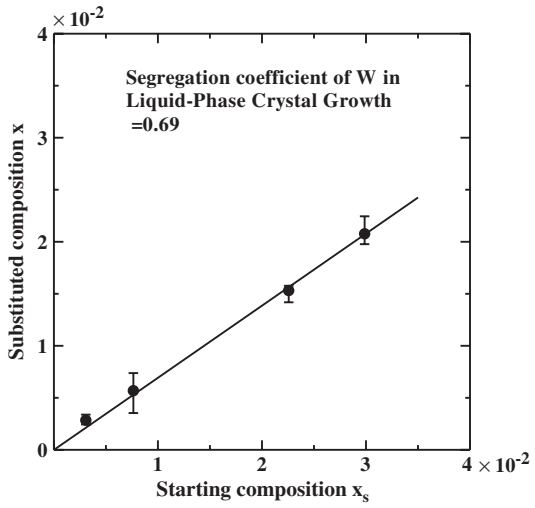

Figure 2. The relationship between starting composition x_s and substituted one x in $W_xV_{1-x}O_2$ by WDS–EPMA. The plots show the average of five measured points for each sample.

we investigate the effect of W doping into VO_2, as W is the most effective dopant for achieving precise control of T_t reduction on an atomic per cent basis [6–9].

In a previous study we used tunnelling spectroscopy to investigate the change in the electronic density of states at the MIT in VO_2 lightly doped with W [10].

In the present study, we use tunnelling spectroscopy to investigate the change in the electronic density of states at the MIT in heavily doped VO_2, in which the resistivity–temperature characteristics show a qualitative change from those in undoped and lightly doped VO_2 samples.

2. Experiments

Crystal growth was carried out using the same method as in the previous study [10]. The crystal structure of the obtained samples was examined by powder x-ray diffraction (XRD) using RAD II–A (Rigaku). One piece of crystal was ground and used for XRD for each W concentration.

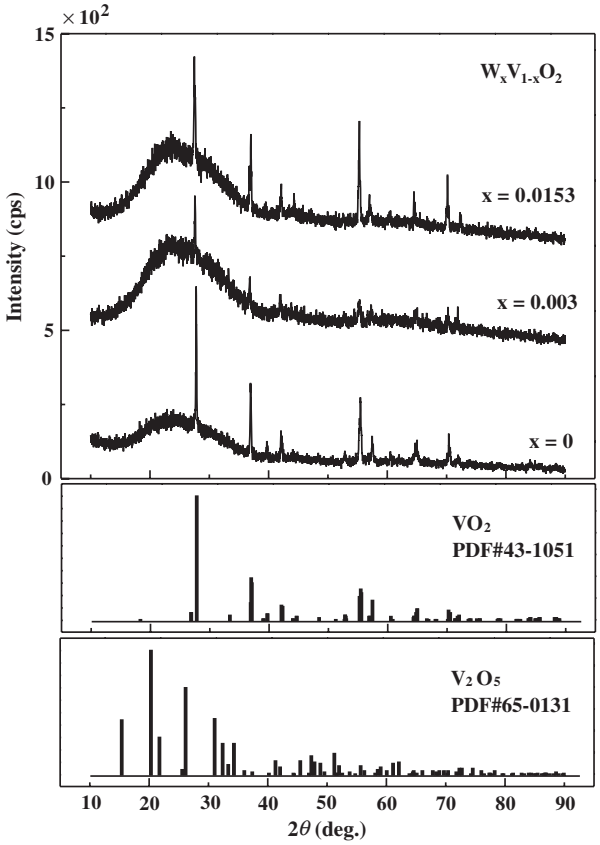

Figure 3. Powder x-ray diffraction patterns of $W_xV_{1-x}O_2$ for $x = 0$, 0.003 and 0.0153. The broad hump around 15°–35° is due to the substrate glass.

The W concentration in the crystal was determined by a wavelength dispersive spectrometer electron probe microanalyser (WDS–EPMA), using JAX-8600 (JEOL). The resolution of the W content was ±0.1%.

Tunnelling measurements were carried out using the planar–contact method as shown schematically in figure 1. The more conventional methods of fabricating tunnel junctions by evaporating or sputtering an insulating material on the sample surface have the possibility of suppressing the structural change accompanying the phase transition at the interface. Moreover, in this planar contact method, the tunnel junction conductance can be adjusted to an appropriate value. The electrical resistance of the tunnel junction was much higher than that of the sample bulk resistance, in series with the tunnel resistance in order to minimize the error in the tunnel bias voltage. The zero bias tunnel junction conductance was adjusted to be 0.5–2.0 mS at room temperature prior to the measurements. Tunnelling spectroscopy was performed using the ac modulation technique with modulation bias of 1 mV and a modulation frequency of 1 kHz. The phase angle between the modulation current and the modulation voltage was about 27° when a test resistor of 1 kΩ was connected to the tunnelling system in place of the sample. When the sample was mounted and the zero bias tunnel conductance was adjusted, the phase angle was 29°–35°. The dI/dV versus V curve did not show any appreciable change when the modulation frequency was changed to 2 and 3 kHz. From these tests, the capacitive component of the sample current is considered to be small.

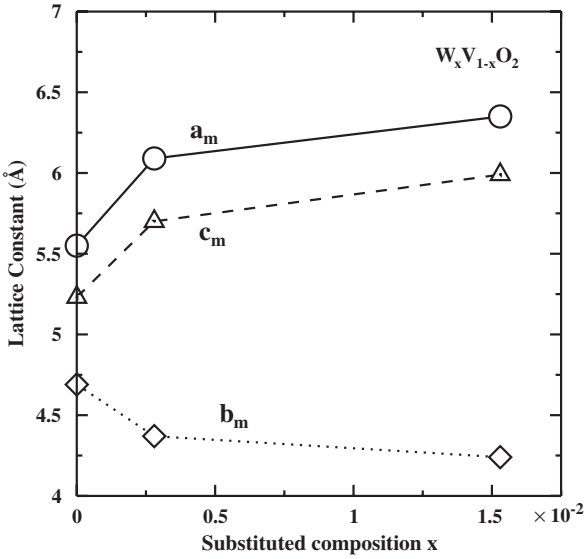

Figure 4. W composition x versus lattice constant in the monoclinic phase of $W_xV_{1-x}O_2$.

In order to estimate the transition temperature and several parameters of the phase transition, the temperature dependence of the electrical resistivity on $W_xV_{1-x}O_2$ with $x = 0$, 0.003, 0.006 and 0.0153 was measured along the c-axis of the rutile type by using a four-probe method.

3. Results and discussion

The W composition x in $W_xV_{1-x}O_2$ was estimated by WDS–EPMA. The relationship between the starting composition and the substituted one is shown in figure 2. Each plot in figure 2 shows the average of the measurements at five different positions on the sample surface and the error bars indicate the range of the five data points. The substituted composition is linearly proportional to the starting composition, and the segregation coefficient is 0.69.

The powder x-ray diffraction patterns of $W_xV_{1-x}O_2$ with various x and the powder diffraction file (PDF) for the reference are shown in figure 3. The XRD patterns of $W_xV_{1-x}O_2$ are as a whole in accordance with the PDF of VO_2, card no.43-1051, and the XRD signals for V_2O_5, which is most likely to coexist with VO_2, were not observed. The lattice constants in the monoclinic structure are shown in figure 4, in which β was fixed at 122.64° in the calculation. With increasing W composition, the lattice constants a_m and c_m show the extension and b_m shows the contraction.

The temperature dependences of the electrical resistivities are shown in figure 5(a). The dependence of T_t on W composition is linear with coefficient -27.8 K/at.% as shown in figure 5(b), in which T_t is plotted for the heating process. The temperature dependence of the resistivity for $x = 0.0153$ is qualitatively different from those for lightly doped samples in the following points. First, the change in resistivity is less sharp at the threshold of the MIT. Second, the electrical resistivities in both temperature phases increase discontinuously from those for lightly doped samples. Third, the temperature dependence in the high-temperature phase has a semiconductor-like characteristic. In table 1, the transition characteristics of $W_xV_{1-x}O_2$ are listed for various x. When the W composition is increased, the ratio of electrical

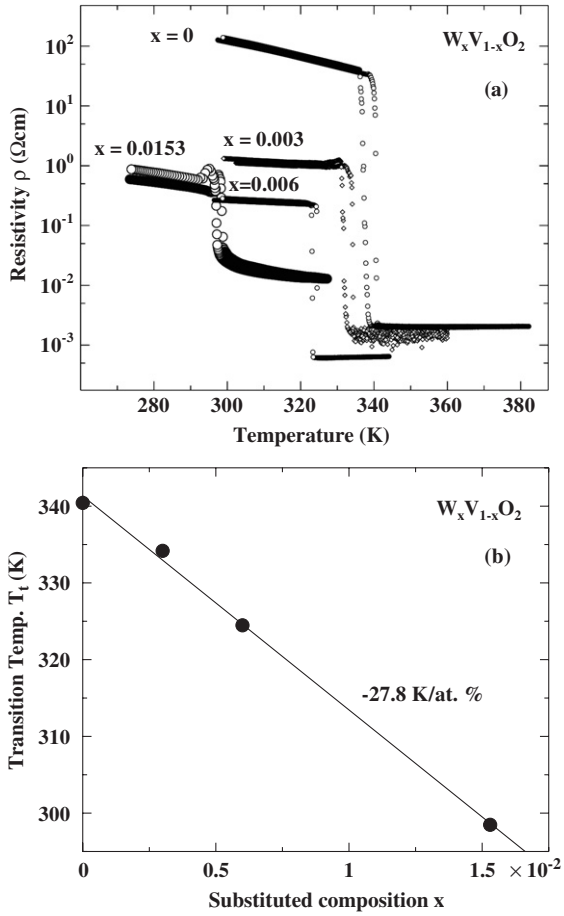

Figure 5. (a) Temperature dependences of electrical resistivities in $W_xV_{1-x}O_2$ for various W compositions x. (b) MIT temperature T_t versus W composition x.

resistivities on both sides of the phase transition is decreased. It is worth noting that the width of the phase transition hysteresis becomes smaller than that for undoped VO_2, which is different from previous reports [11, 12].

In the present study tunnelling spectroscopy was carried out in the heavily W doped sample $W_{0.0153}V_{0.9847}O_2$, and the results are compared with those for lightly doped samples in the previous study.

The tunnelling spectra for $W_{0.0153}V_{0.9847}O_2$ are shown in figure 6. The measurements were made while the temperature was very slowly increasing. The transition temperature (T_t) is 298.5 K, as indicated in table 1. The bias voltage is that of the sample measured against the Al electrode. The scale of dI/dV is common to all experimental curves and the scale of 5 mS is shown in the figure. The curves for above T_t are magnified five times. Each experimental curve is shifted vertically to enable each curve to be seen. At the lowest temperature, 289.0 K, the tunnelling characteristic dI/dV is well symmetric with respect to the polarity of the bias voltage, which indicates that the density of states is symmetric with respect to the Fermi level (E_F). The dI/dV versus V curve below T_t illustrates a pair of pseudo energy gap edges around ± 0.3 eV, and a pair of rising density of states around ± 0.8 eV. When

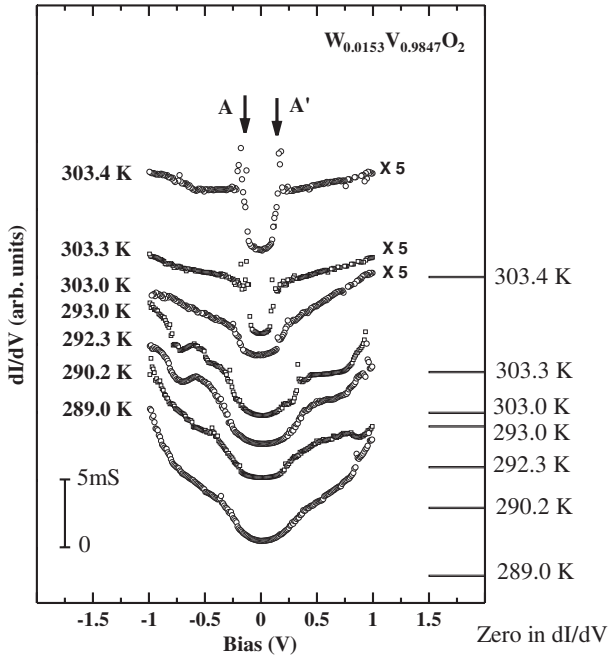

Figure 6. The tunnelling spectra of $W_{0.0153}V_{0.9847}O_2$. The zero position of dI/dV for each temperature is indicated on the right-hand side.

Table 1. Some characteristic parameters in the temperature dependence of electrical resistivity in W doped VO_2. $T_{I\to M}$ and $T_{M\to I}$ are the mid-point temperatures of the MIT during heating and cooling, respectively. $(\rho_I/\rho_M)_{T_t}$ is the ratio of the electrical resistivities on both sides of the transition from insulator to metal. Hysteresis is the separation of temperatures between heating and cooling at the mid-point of the transition.

Sample	W composition x	$T_{I\to M}$ (K)	$T_{M\to I}$ (K)	$(\rho_I/\rho_M)_{T_t}$	Hysteresis (K)
1	Pure	340.4	337.3	1.6×10^4	3.2
2	0.003	334.2	331.7	7.8×10^2	2.5
3	0.006	324.5	323.2	3.4×10^2	1.3
4	0.0153	298.5	297.1	1.7×10^1	1.4

the temperature is increased toward T_t, the density of states around 0.6 eV below E_F increases and that around 0.65 eV above E_F decreases. Such changes in the density of states just below T_t suggest a precursor of the phase transition to the high-temperature phase in heavily doped VO_2. After the phase transition ($T > T_t$), the density of states becomes flat, except that the inner pseudo gap (A, A′ in figure 6) is left and becomes sharper than in the low-temperature phase ($T < T_t$). It contrasts well with the case in a lightly doped sample, where no pseudo-gap structure was observed. The result of the tunnelling spectroscopy in the high-temperature phase of the $W_{0.0153}V_{0.9847}O_2$ sample is in accordance with the semiconductor-like characteristic in the temperature dependence of electrical resistivity, and with that the electrical resistivity in the high-temperature phase is higher than for the samples with smaller x. The slope of the ρ versus $1/T$ curve for the high-temperature phase indicates an intrinsic energy gap of ∼0.44 eV, which is to be compared with the observed pseudo-gap of 0.4–0.5 eV in the high-temperature phase.

If the W doping exceeds a certain level it will introduce a quenched disorder which is negligible for lower doping levels, and will smear the first-order transition. Such effects are observed in the ρ–T curve for $x = 0.0153$. First, the step of change in ρ at the phase transition decreased and became less sharp than for lower doping. Second, the ρ in the low-temperature phase is increased rather than decreased from the lower doping level.

4. Conclusion

Tunnelling spectroscopy was used to examine heavily W doped VO_2, $W_xV_{1-x}O_2$ with $x = 0.0153$. The heavily doped sample showed a temperature dependence of electrical resistivity that was qualitatively different from that for lightly doped samples, which showed a systematic change in MIT characteristics with doping from those in an undoped sample. The behaviour at the MIT in the heavily doped sample was explained by the tunnelling results; a sharp pseudo-energy-gap remained in the high-temperature phase which was not observed in lightly doped samples [10]. The pseudo-gap in the high-temperature phase suggests the introduction of quenched disorder by W doping. A more systematic investigation is to be made on the pseudo-gap in the high-temperature phase.

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