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Phys. Rev. B **91**, 205123 — Published 21 May 2015

DOI: [10.1103/PhysRevB.91.205123](https://doi.org/10.1103/PhysRevB.91.205123)

# Effect of disorder on the metal-insulator transition of vanadium oxides: local versus global effects

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In this paper we investigate the effect of disorder on highly correlated electron systems, which exhibit metal-insulator-transition (MIT) and structural-phase-transition (SPT). We show that the effect of ion irradiation is strikingly different between  $V_2O_3$  and  $VO_2$ , two otherwise similar materials. Upon irradiation, the MIT and SPT temperatures in  $V_2O_3$  decrease drastically at low absolute dosages, much lower than for  $VO_2$ . At a low threshold dose, the insulating state of  $V_2O_3$  drastically collapses into a metallic state. Contrary to this, irradiation of  $VO_2$  leads to a much milder reduction of the MIT and SPT temperatures and to a weak, gradual decrease of the insulating state resistivity – not suppressed even at one order-of-magnitude higher doses than the  $V_2O_3$  threshold. These major differences imply that the phase transition in  $V_2O_3$  arises from global (rather than local as in  $VO_2$ ) physical mechanisms that are extremely sensitive to disorder. This shows that the MIT and SPT may have substantially different physical origins in different systems, with the consequent major implications for theoretical descriptions of the MIT in highly correlated electron systems.

Strong electron correlations in materials [1,2] cause some of the most spectacular properties of solids such as superconductivity [3], colossal magnetoresistance [4], and metal-insulator transition (MIT) observed in a plethora of transition metal oxides [5]. Despite their relevance, electronic correlations are often poorly understood. The MIT in transition metal oxides is experimentally characterized by a several-orders-of-magnitude resistivity change, a coincidental structural phase transition and sometimes magnetic phase transitions. These effects, which may lead to revolutionary applications, have posed a long-standing theoretical challenge [6] (and references therein). Even the most basic issue, whether the microscopic mechanism that produces the MIT is due to short-range (“local”) or long-range (“global”) correlations, is under debate. An example of global correlations is the appearance of long-range order (magnetic or structural), which doubles the unit cell. This in turn opens up a gap at the Fermi surface of a half-filled metallic band [7], giving rise to the MIT. The more “local” correlations giving rise to the MIT arise from the competition between the kinetic energy, which favors electron transport, and the Pauli exclusion-principle, which inhibits electron hopping [8]. Small amounts of disorder may affect differently these two types of electronic mechanisms; i.e. they may disrupt long-range electronic correlations but have only a minor effect on the local ones. An important and crucial issue is therefore whether disorder has the same effect on the MIT of different transition metal oxides. This would clarify whether global or local correlations are operational.

To address this crucial issue we have studied the effects of irradiation-induced disorder in two very similar oxides,  $\text{VO}_2$  and  $\text{V}_2\text{O}_3$ . Both exhibit very similar, large –several orders of magnitude– first order MIT, coincidental with a Structural Phase Transition (SPT) at a stoichiometry-dependent temperature,  $T_C$  [8]. Disorder induced by ion-irradiation has been used in the past in order to fine-control the amount of damage produced [9]. Surprisingly, we found that disorder induced by  $\text{O}^+$  ion irradiation has qualitatively and quantitatively very different

effects in  $V_2O_3$  and  $VO_2$ . While  $VO_2$  is robust,  $V_2O_3$  degrades substantially with two orders of magnitude smaller irradiation doses. The insulating state resistivity of  $V_2O_3$  remains constant initially, while the  $T_C$  starts decreasing at the smallest doses. Above a small threshold dose, the insulating state abruptly collapses and the resistivity decreases by six orders of magnitude. Contrary to this, even with two orders of magnitude higher irradiation doses, the  $VO_2$   $T_C$  drops only slightly. Moreover, the insulating state is preserved with only a gradual reduction of its resistivity. This shows that the SPT and MIT are much more sensitive to disorder in  $V_2O_3$  than in  $VO_2$ , which implies that global effects play a more important role in  $V_2O_3$  than in  $VO_2$ . These observations have important implications for theories being developed to understand the MIT [10,11], especially regarding the role of long range versus local correlations. These results unambiguously illustrate the unexpected, strikingly different nature of the electronic correlations in two otherwise very similar materials.

$V_2O_3$  and  $VO_2$  thin films were deposited on R-plane sapphire substrates by RF magnetron sputtering [12]. More details on sample preparation are elsewhere [13-15]. In as-grown  $V_2O_3$  [Fig. 1(a)] the out-of-plane, rhombohedral (012) X-ray diffraction (XRD) peak shifts from  $2\theta = 24.30^\circ$  above the SPT (300 K) to the monoclinic (011) [16]  $2\theta = 24.05^\circ$  below it (100 K) [17]. For  $VO_2$  [Fig. 1(b)], the shift is from  $2\theta = 37.26^\circ$  at 360 K to  $2\theta = 37.10^\circ$  at 300 K, which corresponds to the tetragonal (101) to monoclinic (200) SPT [2]. During the SPT (around  $\sim 170$  K for  $V_2O_3$  and  $\sim 328$  K for  $VO_2$ ) the diffracted intensity is gradually redistributed between the two diffraction angles corresponding to the different lattice parameters of the two structural phases [Fig. 1(a) and (b)]. The virgin SPT and MIT temperatures can vary by  $\pm 5$  K from sample to sample, which is substantially smaller than the effects observed due to  $O^+$  irradiation.

Temperature dependent electrical transport was performed in all samples. As-grown  $V_2O_3$  shows a 6 orders of magnitude change in resistivity at  $T_C \sim 165$  K [black curves in Fig. 2(a)-(d)].

As grown VO<sub>2</sub> shows a 4 orders of magnitude change in resistivity at T<sub>C</sub> ~ 348 K [black curves in Fig. 2(e)-(f)] [12].

Following the initial characterizations, each of the V<sub>2</sub>O<sub>3</sub> and VO<sub>2</sub> films was irradiated with O<sup>+</sup> ions at doses ranging between 5×10<sup>12</sup> to 2×10<sup>15</sup> ions/cm<sup>2</sup>, at a constant 110 keV energy. A “low” flux of ~1.5×10<sup>12</sup> ions s<sup>-1</sup> cm<sup>-2</sup> was used to avoid sample heating during irradiation. SRIM simulations [18] of the ion damage in both materials were performed, assuming the same 30 keV threshold displacement energy for all atomic species. The simulations show that most of the oxygen ions traverse the thin film and reach the substrate: at most 10 % of the ions are implanted in the vanadium oxide. Even for the highest dose 2×10<sup>15</sup> ions/cm<sup>2</sup>, the expected oxygen content increase due to implantation is only ~0.1%, which can be neglected. The evolution of the XRD and of the metallic-state resistivity with increasing irradiation dose [see discussion below Fig 1(c)-(d) and Fig. 3(c)] suggest that, both in VO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub>, the irradiation damage produces a non-saturating accumulation of sub-nanometric clusters or quasi point defects [12].

The very same samples were investigated after ion irradiation using quantitative structural and transport measurements as described above. Fig. 1(c) and (d) respectively show a series of θ–2θ XRD diffraction data for V<sub>2</sub>O<sub>3</sub> and VO<sub>2</sub> films irradiated with different doses. The XRD spectra of as-grown samples are included for comparison. For each dose, the high-temperature XRD above the SPT (red line) is compared to the low-temperature one below the SPT (blue symbols).

The first remarkable observation is that both materials preserve their high-temperature crystal structure under irradiation, as indicated by the absence of a significant change in the XRD [red line, Fig. 1(c) and (d)]. After irradiation a shift in 2θ is observed at room temperature which reaches 0.10° for V<sub>2</sub>O<sub>3</sub> and Δ2θ ~ 0.23° for VO<sub>2</sub>. These shifts are similar to differences in 2θ observed among different samples and therefore considered to be insignificant. The diffraction peak width is unaffected by the irradiation and in-plane measurements (not shown) confirm that

all crystal symmetries are preserved. No signs of amorphization appeared in the XRD spectra after irradiation. All of the above is a clear indication that, for both materials, the  $O^+$  irradiation does not induce major structural changes even at the highest doses, which suggests that the ion damage creates point defects and/or sub-nanometric defect clusters [12].

Fig. 1(c) shows that the  $V_2O_3$  SPT is observable only below  $2 \times 10^{14}$  ions/cm<sup>2</sup>: above this dose the structure remains in the rhombohedral symmetry [19] at all temperatures. Contrary to this, for  $VO_2$  the SPT is observed for all doses, even at the highest  $2 \times 10^{15}$  ions/cm<sup>2</sup> [Fig. 1(d)]. The diffraction data show that the SPT hysteresis widens with increasing dose. No trace of residual insulating (metallic) phases are observed at temperatures well below (above) the phase transition, indicating that the SPT and the reduction in transition temperature is homogeneous across the sample.

The effect of irradiation on the transport properties of  $V_2O_3$  [Fig. 2(a)-(d)] and  $VO_2$  [Fig. 2(e)-(f)] is drastically different between the two materials.

For  $V_2O_3$ ,  $T_C$  is markedly reduced with increasing dose [red curves in Fig. 2(a)-(c)]. A clear shift of the  $T_C$  is found even for the lowest dose  $5 \times 10^{12}$  ions/cm<sup>2</sup> [Fig. 2(a)]. On the other hand, the resistivity change at the MIT essentially remains unchanged with increasing dose until a  $2 \times 10^{14}$  ions/cm<sup>2</sup> threshold is reached. Then a drastic (six orders of magnitude) collapse of the resistivity takes place [see Fig. 2(d)] and only a small transition ( $\sim 10^{-4}$   $\Omega$  cm) remains below 60 K [see inset Fig. 2(d)].

$VO_2$  shows a much milder decrease in  $T_C$  with increasing dose [blue curves in Fig. 2(e)-(h)] similarly to the SPT [Fig. 1(d)]. Only a small (a few Kelvin)  $T_C$  decrease occurs at around 100 times higher doses than for  $V_2O_3$ . On the other hand, the MIT is not suppressed even for the highest doses: a two orders of magnitude MIT remains at  $2 \times 10^{15}$  ions/cm<sup>2</sup>.

A quantitative comparison between the irradiation effects on  $V_2O_3$  and  $VO_2$  is shown in Fig 3. To characterize the irradiation effect on the resistivity change at the MIT, we define the

“MIT magnitude”  $\Delta\rho \equiv \log(\rho_I/\rho_M)$ , where the high-temperature (metallic-state)  $\rho_M$  and low-temperature (insulating-state)  $\rho_I$  resistivities are taken at the temperatures at which the loop closes. Fig. 3(a) shows  $\Delta\rho^{ID}/\Delta\rho$  for both  $V_2O_3$  and  $VO_2$ , with  $\Delta\rho$  and  $\Delta\rho^{ID}$  the MIT magnitude before and after irradiation damage (ID). Strikingly, the  $\Delta\rho^{ID}/\Delta\rho$  decrease for  $V_2O_3$  (circles) is sharp and occurs at a well-defined threshold dose, whereas  $VO_2$  (squares) shows a much more gradual decrease. Furthermore, at the doses at which the MIT is fully suppressed for  $V_2O_3$ , the MIT magnitude decreases by only 20-50 % in  $VO_2$ .

The irradiation effects on the MIT and SPT transition temperature are shown in Fig. 3(b). The horizontal shaded regions indicate the transition temperatures of the as-grown samples. For  $V_2O_3$  a drastic reduction of the MIT temperature (10 K) is found even at the lowest dose and for  $5 \times 10^{13}$  ions/cm<sup>2</sup> the reduction reaches almost 70 K. This is in stark contrast with the much milder effects observed in  $VO_2$ , for which the reduction is only of 5 K at  $2 \times 10^{14}$  ions/cm<sup>2</sup> and 16 K for the highest dose  $2 \times 10^{15}$  ions/cm<sup>2</sup>.

The relative change in the metallic-phase resistivity upon irradiation,  $\rho_M^{ID}/\rho_M$ , is qualitatively similar in both oxides [Fig. 3(c)]. At low doses the resistivity is essentially constant, and a gradual increase is observed above  $\sim 10^{14}$  ions/cm<sup>2</sup> for both materials. This is expected if the increasing dose leads to a proportionally higher concentration of defects –either point defects and/or very small sub-nanometric defects clusters– and thus to a shorter electronic mean free path. This implies that the defect creation does not saturate in the high-dose range, in agreement with earlier experiments in similar systems [19,20]. The resistivity increase is slightly higher in  $VO_2$  (squares) than in  $V_2O_3$  (circles), which suggests that a higher defect density in the former than in the latter. This is in stark contrast with the fact that the irradiation effects on the MIT and SPT are considerably stronger in  $V_2O_3$  than in  $VO_2$ .

Furthermore, we have ruled out the effect of charge doping by comparing the expected increase of oxygen content from SRIM simulations (around 0.1% approx. for the highest dose)

with existent literature values. For instance, in order to change the  $T_C$  value by 10 K, the chemical substitution or the increase of the oxygen content has to be around 1% for both  $\text{VO}_2$  [7,21] and  $\text{V}_2\text{O}_3$  [22,24]. This is far from the 0.1% we obtained from SRIM simulations and suggests that the irradiation damage does not produce significant chemical doping but a non-saturating accumulation of sub-nanometric clusters or quasi point defects [12].

In summary, while the XRD and electrical transport studies show that  $\text{O}^+$  irradiation produces only minor structural changes at room temperature and an increase in the metallic-state resistivity –both for  $\text{VO}_2$  and  $\text{V}_2\text{O}_3$ – the effects on the MIT and SPT are quite striking and very different between the two materials:

1.  $\text{VO}_2$  is much less affected by irradiation than  $\text{V}_2\text{O}_3$ . The doses needed to get an observable effect on the  $\text{VO}_2$  MIT and SPT are a factor of  $\sim 100$  larger than for  $\text{V}_2\text{O}_3$ .
2. In  $\text{V}_2\text{O}_3$  the  $T_C$  starts dropping from the minimal dose, whereas in  $\text{VO}_2$   $T_C$  remains more or less constant in comparison, even for higher absolute doses.
3. In  $\text{V}_2\text{O}_3$  the resistivity change at the MIT is robust up to a threshold where a drastic drop occurs. Contrarily, in  $\text{VO}_2$  the resistivity gradually decreases and the MIT is not suppressed even for 100 times higher doses.

All of the above leads to an inescapable, interesting, qualitative conclusion: the MIT and SPT in  $\text{V}_2\text{O}_3$  are much more sensitive to disorder than in  $\text{VO}_2$ . This conclusion clearly should play a major role in the theoretical understanding of the MIT in these materials, especially considering that disorder is always present and unavoidable in them.

Several possible theoretical explanations have been advanced for the MIT in transition metal oxides, vanadium oxides in particular. In general, it is not clear whether the MIT is caused by the SPT or whether strong correlations drive both transitions [25,26]. Many theories rely on the opening of a collective gap in the half-filled metallic conduction-band due to the doubling of the



unit cell. This can be caused by global effects, such as structural distortions (“Peierls”) due to the formation of V-V dimers in VO<sub>2</sub> [6], or antiferromagnetic order (“Slater”) for instance suggested in V<sub>2</sub>O<sub>3</sub> [27]. A more local description relies on the Hubbard Hamiltonian, such as expected for a “Mott-Hubbard” insulator [8]. In the latter model the MIT arises from the competition between the kinetic energy, which favors electron transport, and the Pauli exclusion principle, which inhibits electron hopping. These types of local effects are supported for instance by NMR and EPR experiments in VO<sub>2</sub> with Cr doping [28] or uniaxial pressure [29]. Based on a series of Ti and Cr doping experiments, it was also claimed that pure V<sub>2</sub>O<sub>3</sub> (without doping) becomes insulating because of a Mott transition [29,30]. If the same mechanism drives the MIT in VO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub>, the effect of disorder should be the same in both materials. However, the major experimental differences observed here between these two otherwise similar oxides imply that in each of them different (or additional) mechanisms must be playing a crucial role. It is indeed possible that several mechanisms act together, as it is presumably the case for VO<sub>2</sub>, where dimer formation produces a Peierls transition which may at the same time “assist” the Mott mechanism by reducing the electron kinetic energy [32].

The large differences in the sensitivity of the electrical transport to irradiation damage show that quite similar systems may exhibit very different mechanisms for the development of the MIT. Particularly the insensitivity to irradiation damage of the MIT in VO<sub>2</sub> seems to arise from a much more local origin than in V<sub>2</sub>O<sub>3</sub>. Therefore, the insulating phase of VO<sub>2</sub> has much more Mott-Hubbard character than V<sub>2</sub>O<sub>3</sub>. The experimental results described above are indeed in agreement with these recent theoretical calculations, which have claimed that the Mott transition assisted by the Peierls instability should be insensitive to the presence of disorder [32]. On the other hand, the extreme sensitivity of V<sub>2</sub>O<sub>3</sub> to disorder suggests that in this material a long-range global mechanism –for instance the Slater transition associated to antiferromagnetic order– plays a dominant role.

In summary, a systematic structural and transport study comparing the effect of  $O^+$  irradiation shows that the insulating state and the MIT of  $VO_2$  are much more robust and less susceptible to disorder than for  $V_2O_3$ . Structural measurements, on the other hand, are insensitive to irradiation with  $O^+$  ions, thus indicating that no major structural changes or formation of secondary phases occur. The striking and qualitatively different responses to  $O^+$  irradiation in the transport show that the formation of the MIT and SPT in  $VO_2$  are dominated by local properties, whereas in  $V_2O_3$  global effects play a more important role.

Research at University of California San Diego is supported by AFOSR Grant No. FA9550-12-1-0381. JEV acknowledges support from EU-FP7, which financed via IRSES “COEF-magNANO” a stay at UCSD during which these experiments were designed. The authors acknowledge useful discussions with H. Bernas, G. Kotliar, L. Pizzagalli, M. Rozenberg and K. Haule. JGR acknowledges useful discussions with A. Sharoni, and J-P C thanks Thomas Jourdan and Alain Chartier for fruitful discussions. One of us (IKS) thanks D. Ravelosona, M. Viret and J. E. Villegas for their hospitality during a sabbatical stay where many ideas were generated and this manuscript was written. Financial support for this sabbatical stay was financed by the RTRA “Triangle de la Physique”. J. T. acknowledges Fundación Barrié for a PhD fellowship.

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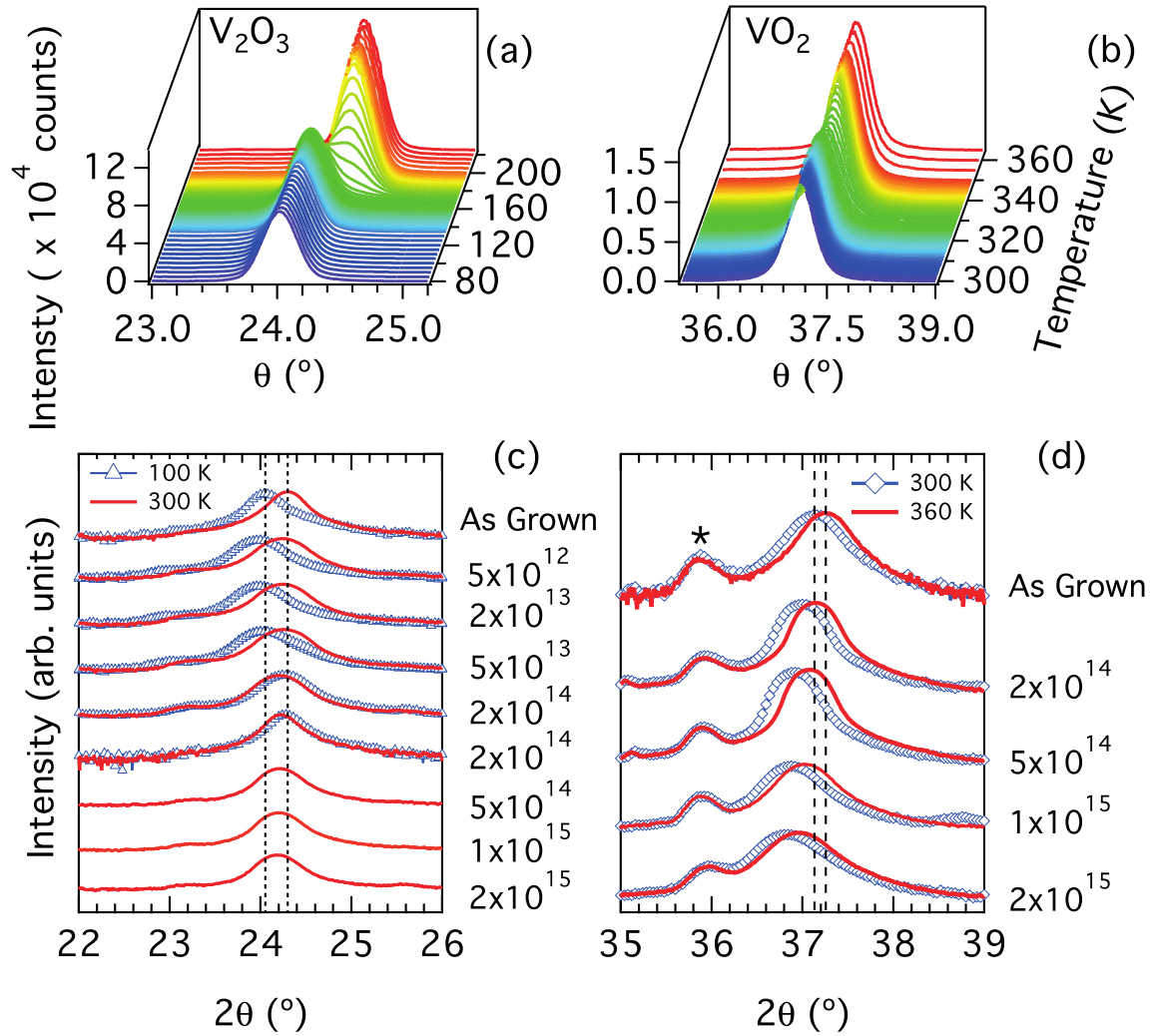


FIG. 1. (color online). (a) and (b) XRD at different temperatures across the SPT for  $V_2O_3$  and  $VO_2$ , respectively. (c) and (d) XRD at two different temperatures and different doses as indicated (dose in units of  $\text{ion}/\text{cm}^2$ ). The curves in (c) and (d) are shifted along the vertical axes for clarity. Upper curves on both panels correspond to non-irradiated reference samples measured under the same experimental conditions. Peaks marked with (\*) belong to the sample holder.

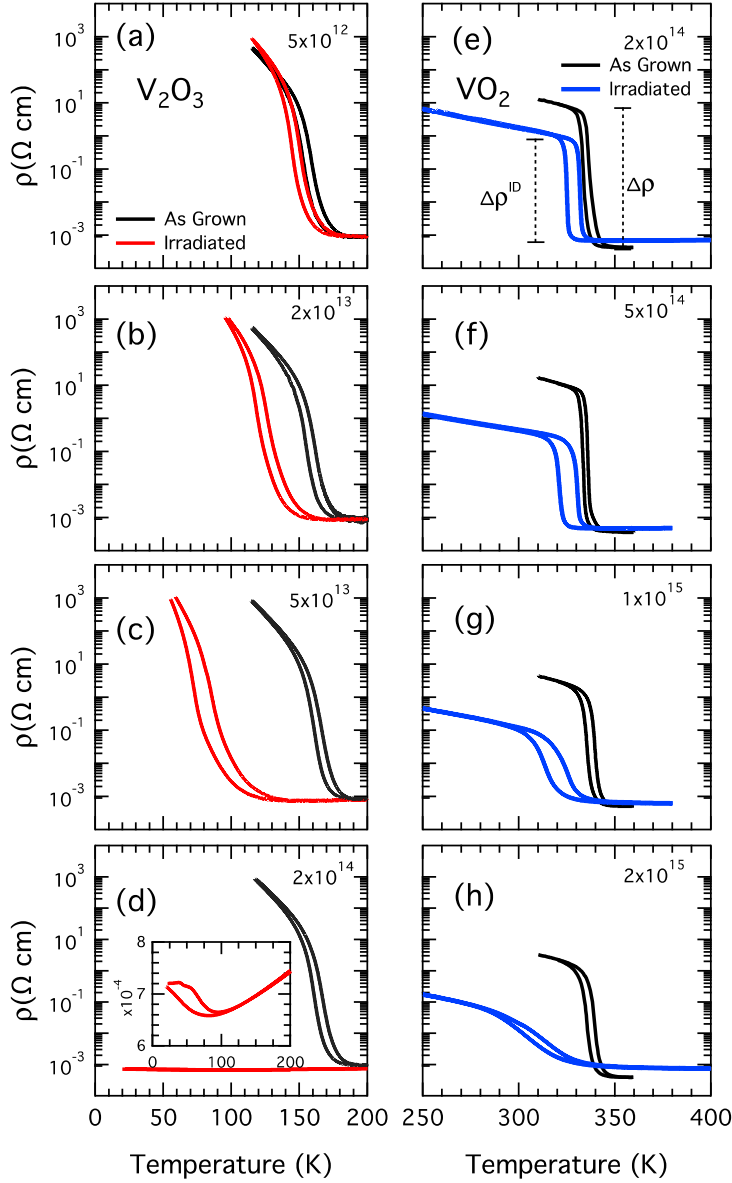


FIG. 2. (color online). Resistivity as a function of temperature for (a)-(d)  $V_2O_3$  and (e)-(h)  $VO_2$  as-grown films (black solid lines) and after oxygen irradiation (red solid lines for  $V_2O_3$  and blue solid lines for  $VO_2$ ). Note the different doses used as indicated inside the plot. The definition of the resistivity changes  $\Delta\rho$  and  $\Delta\rho^{ID}$  (see text) is indicated in (e). Inset on (d) depicts the post-irradiated resistivity in linear scale.

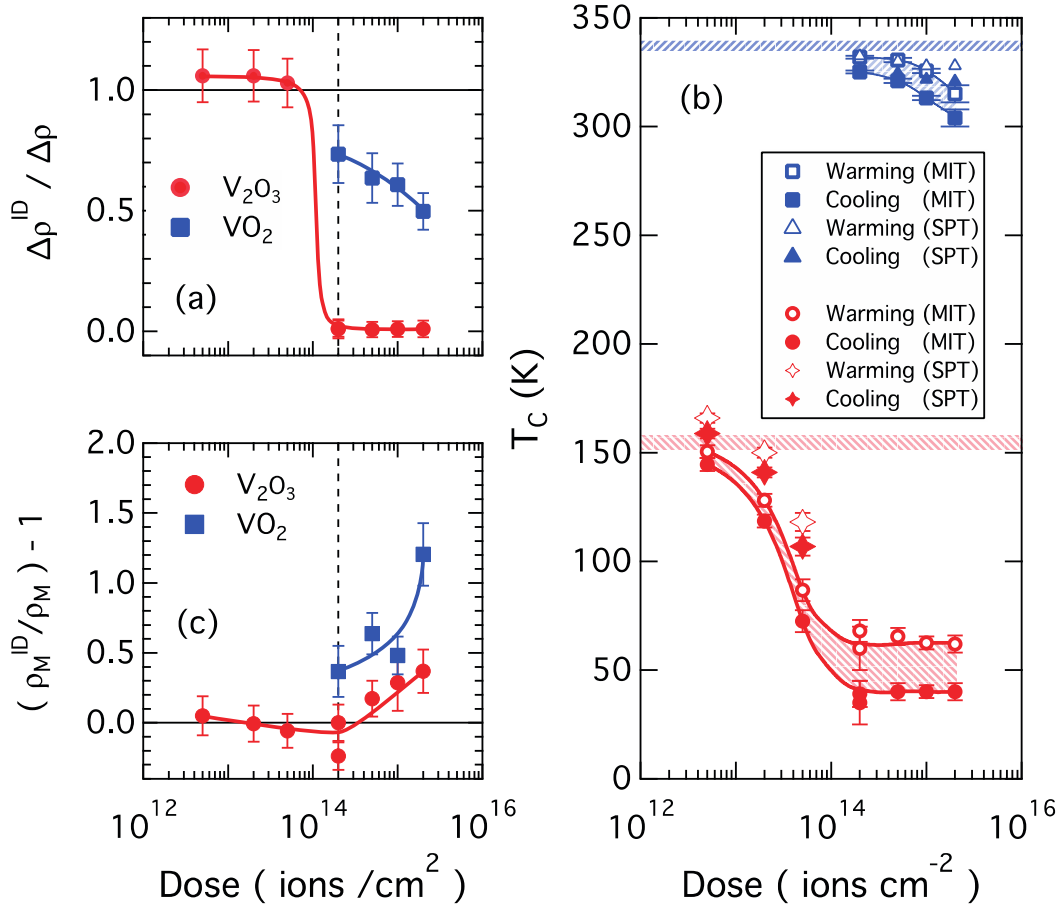


FIG. 3. (color online) (a) Relative change of the resistivity calculated as  $\Delta\rho^{ID}/\Delta\rho$  for  $V_2O_3$  (circle) and  $VO_2$  (square). The dashed line marks the  $2.0 \times 10^{14}$  ions/cm<sup>2</sup> dose threshold. (b) Transition temperature obtained from curves in Figure 2 after irradiation, for  $VO_2$  (upper) and  $V_2O_3$  (lower). Values from the cooling and heating branches are presented and the hysteretic region is indicated. The solid lines are guides to the eye. (c) Metallic state resistivity  $\rho_M^{ID}$  as a function of the irradiation dose for  $VO_2$  and  $V_2O_3$ , normalized to the resistivity prior to irradiation  $\rho_M$ .

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