

# Chromium niobium co-doped vanadium dioxide films: Large temperature coefficient of resistance and practically no thermal hysteresis of the metal insulator transition

著者別名	藤田 淳一
journal or publication title	AIP Advances
volume	6
number	5
page range	055012
year	2016-05
権利	(C) 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license ( <a href="http://creativecommons.org/licenses/by/4.0/">http://creativecommons.org/licenses/by/4.0/</a> ).
URL	<a href="http://hdl.handle.net/2241/00143391">http://hdl.handle.net/2241/00143391</a>

doi: 10.1063/1.4949757



## Chromium–niobium co-doped vanadium dioxide films: Large temperature coefficient of resistance and practically no thermal hysteresis of the metal–insulator transition

Kenichi Miyazaki, Keisuke Shibuya, Megumi Suzuki, Kenichi Sakai, Jun-ichi Fujita, and Akihito Sawa

Citation: *AIP Advances* **6**, 055012 (2016); doi: 10.1063/1.4949757

View online: <http://dx.doi.org/10.1063/1.4949757>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/adva/6/5?ver=pdfcov>

Published by the *AIP Publishing*

---

### Articles you may be interested in

Electrical and optical characterization of the metal-insulator transition temperature in Cr-doped VO<sub>2</sub> thin films  
*J. Appl. Phys.* **113**, 173704 (2013); 10.1063/1.4803551

Low-temperature oriented growth of vanadium dioxide films on CoCrTa metal template on Si and vertical metal–insulator transition

*J. Vac. Sci. Technol. A* **30**, 051502 (2012); 10.1116/1.4733995

Metal-insulator transition sustained by Cr-doping in V<sub>2</sub>O<sub>3</sub> nanocrystals

*Appl. Phys. Lett.* **100**, 043103 (2012); 10.1063/1.3679396

Mg doping of thermochromic VO<sub>2</sub> films enhances the optical transmittance and decreases the metal-insulator transition temperature

*Appl. Phys. Lett.* **95**, 171909 (2009); 10.1063/1.3229949

Influence of ambient atmosphere on metal-insulator transition of strained vanadium dioxide ultrathin films

*J. Appl. Phys.* **100**, 063714 (2006); 10.1063/1.2345600

---

Searching? Trust CISE.

It's peer-reviewed and appears in the IEEE Xplore and AIP library packages.

## Chromium–niobium co-doped vanadium dioxide films: Large temperature coefficient of resistance and practically no thermal hysteresis of the metal–insulator transition

Kenichi Miyazaki,<sup>1,2,a</sup> Keisuke Shibuya,<sup>3,a</sup> Megumi Suzuki,<sup>1</sup> Kenichi Sakai,<sup>1</sup> Jun-ichi Fujita,<sup>2</sup> and Akihito Sawa<sup>3</sup>

<sup>1</sup>Denso Corporation, Aichi 470-0111, Japan

<sup>2</sup>University of Tsukuba, Tsukuba 305-8571, Japan

<sup>3</sup>National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan

(Received 10 March 2016; accepted 3 May 2016; published online 10 May 2016)

We investigated the effects of chromium (Cr) and niobium (Nb) co-doping on the temperature coefficient of resistance (TCR) and the thermal hysteresis of the metal–insulator transition of vanadium dioxide (VO<sub>2</sub>) films. We determined the TCR and thermal-hysteresis-width diagram of the V<sub>1-x-y</sub>Cr<sub>x</sub>Nb<sub>y</sub>O<sub>2</sub> films by electrical-transport measurements and we found that the doping conditions  $x \gtrsim y$  and  $x + y \geq 0.1$  are appropriate for simultaneously realizing a large TCR value and an absence of thermal hysteresis in the films. By using these findings, we developed a V<sub>0.90</sub>Cr<sub>0.06</sub>Nb<sub>0.04</sub>O<sub>2</sub> film grown on a TiO<sub>2</sub>-buffered SiO<sub>2</sub>/Si substrate that showed practically no thermal hysteresis while retaining a large TCR of 11.9%/K. This study has potential applications in the development of VO<sub>2</sub>-based uncooled bolometers. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4949757>]

### I. INTRODUCTION

Vanadium oxides exhibit a temperature-induced metal–insulator transition (MIT) with a discontinuous change in electrical conductivity of several orders of magnitude.<sup>1</sup> The MIT is the first-order structural transition and is also accompanied by a marked change in the optical transmittance in the infrared (IR) region. Among the various oxides of vanadium, vanadium dioxide (VO<sub>2</sub>) is the most interesting from an application perspective because its MIT occurs at around 340 K, which is above room temperature.<sup>2</sup> An MIT above room temperature is useful in a variety of functional devices, such as electrical switches, gas sensors, smart windows, uncooled bolometers, or thermal memories.<sup>3</sup> Among these devices, VO<sub>2</sub>-based uncooled bolometers that detect far-IR radiation have been actively studied and developed for several decades.<sup>4–8</sup>

One measure of the suitability of a material for use in a bolometer is its temperature coefficient of resistance (TCR), which is defined as  $|(1/\rho)(d\rho/dT)|$ , where  $\rho$  is the resistivity or resistance and  $T$  is the temperature of the material. The TCR value of VO<sub>2</sub> reaches more than 70%/K near the MIT temperature ( $T_{MI}$ ),<sup>9</sup> which is more than ten times that of conventional uncooled bolometer materials such as Si or Ge.<sup>10–12</sup> However, VO<sub>2</sub> shows a large thermal hysteresis in the  $\rho$ – $T$  curve across the MIT. The hysteretic behavior indicates the coexistence of two phases over a finite temperature range due to superheating and supercooling effects, which is a characteristic of the first-order transition. The thermal hysteresis in the  $\rho$ – $T$  curve results in poor measurement reproducibility in IR sensing. Consequently, thermal hysteresis has to be minimized to realize high-sensitivity uncooled bolometers based on VO<sub>2</sub>.

<sup>a</sup>Authors to whom correspondence should be addressed. Electronic addresses: [kenichi\\_miyazaki@denso.co.jp](mailto:kenichi_miyazaki@denso.co.jp) and [k.shibuya@aist.go.jp](mailto:k.shibuya@aist.go.jp)



Doping of VO<sub>2</sub> with metal ions has been employed as a means of suppressing its thermal hysteresis;<sup>13,14</sup> however, doping with metal ions also gives rise to a reduction in the TCR of VO<sub>2</sub>. We previously conducted a systematic study of the TCR and thermal hysteresis in VO<sub>2</sub> doped with Cr or with Nb, and we found that there is a correlation between the TCR and thermal hysteresis, which is independent of the doping element.<sup>15</sup> Our findings implied that a high TCR and the absence of thermal hysteresis were difficult to achieve simultaneously in single-element doped VO<sub>2</sub>. However, Soltani *et al.* reported that co-doping of VO<sub>2</sub> with Ti and W suppresses thermal hysteresis more effectively than does doping with W alone.<sup>16</sup> In their study, they simultaneously achieved a practical absence of thermal hysteresis and a TCR of 5.12%/K at room temperature in V<sub>0.866</sub>W<sub>0.014</sub>Ti<sub>0.12</sub>O<sub>2</sub> films. This TCR is larger than that of conventional uncooled bolometer materials. However, it is still challenging to achieve the high TCR values in excess of 10%/K that are required for high-sensitivity uncooled bolometers.

In this study, we explored the possibility of obtaining high TCR values with no thermal hysteresis by co-doping VO<sub>2</sub> films with Cr and Nb. Note that V, Cr, and Nb ions are tetravalent (4+), trivalent (3+), and pentavalent (5+), respectively, and that their effective radii are 0.058, 0.062, and 0.064 nm, respectively. We previously reported that Nb doping is effective in reducing the thermal hysteresis of VO<sub>2</sub>;<sup>15</sup> however, it also causes a rapid decrease in its TCR. In contrast, the decrease in the TCR of VO<sub>2</sub> on doping with Cr is moderate, but Cr doping is less effective than Nb doping in reducing the thermal hysteresis. These differing effects on the TCR and thermal hysteresis might be due to the differences in the valence states and/or ionic radii of the Cr and Nb ions.<sup>15</sup> Because Cr and Nb dopants are effective in maintaining large TCR values and in reducing the thermal hysteresis, respectively, co-doping with Cr and Nb might give rise to a combination of the desirable effects of the two individual ions.

From  $\rho$ - $T$  measurements on the V<sub>1-x-y</sub>Cr<sub>x</sub>Nb<sub>y</sub>O<sub>2</sub> films, we derived a TCR and thermal-hysteresis-width ( $\Delta T_{MI}$ ) diagram for the films. This diagram revealed that doping conditions of  $x \geq y$  and  $x + y \geq 0.1$  are suitable for producing films that show no thermal hysteresis while retaining a large TCR. We also succeeded in producing a large TCR of 11.9%/K and practically no thermal hysteresis in V<sub>0.90</sub>Cr<sub>0.06</sub>Nb<sub>0.04</sub>O<sub>2</sub> films fabricated on TiO<sub>2</sub>-buffered SiO<sub>2</sub>/Si substrates at process temperatures below 670 K.

## II. EXPERIMENTAL

V<sub>1-x-y</sub>Cr<sub>x</sub>Nb<sub>y</sub>O<sub>2</sub> films were grown on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) single-crystal substrates and TiO<sub>2</sub>/SiO<sub>2</sub>/Si (100) substrates by pulsed-laser deposition with a KrF excimer laser ( $\lambda = 248$  nm). Mixed ceramic pellets consisting of V<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>3</sub>, and Nb<sub>2</sub>O<sub>5</sub> were used as targets. The doping range for Cr was  $x = 0$ –0.12 and that of Nb was  $y = 0$ –0.09. We have previously described the detailed conditions for growth of such films on Al<sub>2</sub>O<sub>3</sub><sup>15</sup> or TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrates.<sup>17</sup> The film thickness was set at 70–110 nm, as confirmed by using a surface profiler. Note that there were no significant differences in the structural or electronic properties of the films within this thickness range. The resistivity of the films was measured by conventional four-probe methods using Ti/Au electrodes. Transport properties were examined by using a physical property measurement system (PPMS; Quantum Design), and the temperature sweep rate was set to 0.3 K/min.

## III. RESULTS AND DISCUSSIONS

Figures 1(a) and 1(b) show the  $\rho$ - $T$  curves for the V<sub>0.95-x</sub>Cr<sub>x</sub>Nb<sub>0.05</sub>O<sub>2</sub> and V<sub>0.95-y</sub>Cr<sub>0.05</sub>Nb<sub>y</sub>O<sub>2</sub> films on Al<sub>2</sub>O<sub>3</sub> substrates with  $0 \leq x \leq 0.12$  and  $0 \leq y \leq 0.08$ , respectively. As a reference, the  $\rho$ - $T$  curve for a nondoped VO<sub>2</sub> film is also shown in Fig. 1(b). A systematic change in  $T_{MI}$  with doping was observed. Here,  $T_{MI}$  is defined as the halfway point between the temperatures of the two peaks in the TCR for the heating and cooling processes, respectively. In addition to the change in  $T_{MI}$ , the doping affected the values of the TCR and  $\Delta T_{MI}$ . The co-doped films showed a broadening of the MIT, and the change in  $\rho$  across the MIT for the co-doped films was smaller than that for the

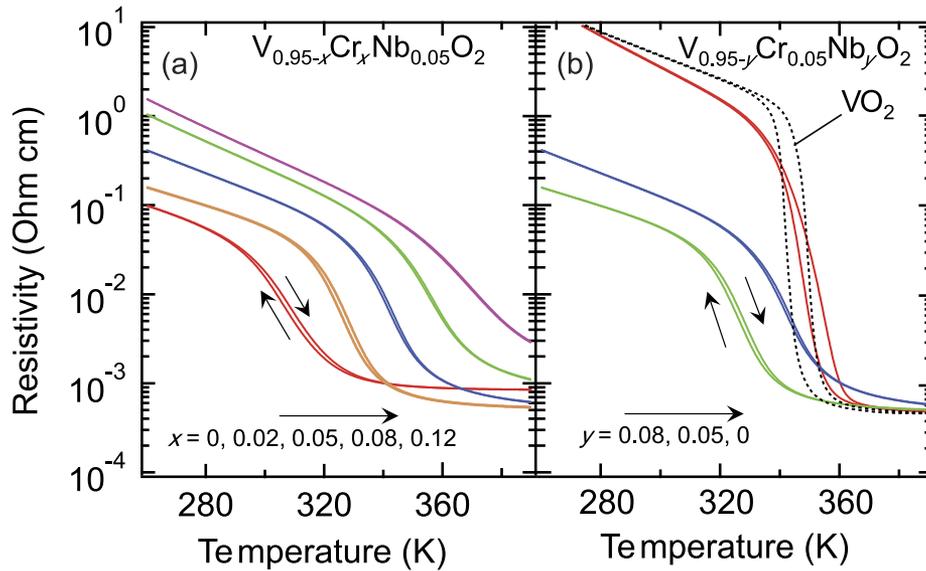


FIG. 1. Temperature dependence of the resistivity of (a)  $V_{0.95-x}Cr_xNb_{0.05}O_2$  and (b)  $V_{0.95-y}Cr_{0.05}Nb_yO_2$  films. As a reference, the  $\rho$ - $T$  curve for the nondoped  $VO_2$  film (dashed line) is plotted in (b).

nondoped film. These behaviors caused a decrease in the TCR of the co-doped films. Moreover, the co-doped films had a smaller  $\Delta T_{MI}$  compared with the nondoped film.

Figure 2(a) and 2(b) show the dependence of  $T_{MI}$ , the maximum TCR, and  $\Delta T_{MI}$  on the total dopant content  $x + y$  for the  $V_{0.95-x}Cr_xNb_{0.05}O_2$  and  $V_{0.95-y}Cr_{0.05}Nb_yO_2$  films on  $Al_2O_3$  substrates, respectively. The results of single-element doping<sup>16</sup> are also plotted for comparison. It is well known that hole doping by lower-valence elements such as  $Cr^{3+}$  or  $Al^{3+}$  raises the  $T_{MI}$ , whereas electron doping with higher-valence elements such as  $Nb^{5+}$  or  $W^{6+}$  lowers the  $T_{MI}$ .<sup>15,18-20</sup> These tendencies are maintained in co-doped  $VO_2$ . As seen in the top panels in Fig. 2, an increase in the Cr content raised the  $T_{MI}$  of the  $V_{0.95-x}Cr_xNb_{0.05}O_2$  films, whereas an increase in the Nb content reduced the  $T_{MI}$  of the  $V_{0.95-y}Cr_{0.05}Nb_yO_2$  films. The  $T_{MI}$  of the  $V_{0.90}Cr_{0.05}Nb_{0.05}O_2$  ( $x = y = 0.05$ ) film was almost identical to that of the nondoped  $VO_2$  film. These results can be explained in terms of the valence state  $A+$  of the V ions, which can be defined as  $A = 4 + x - y$ . The  $T_{MI}$  of the co-doped films is dominated by the valence state of the V ions.

Doping of  $VO_2$  with metal ions generally induces a broadening of the MIT, resulting in a decrease in the TCR. This behavior can be understood in terms of a spatial variation in the  $T_{MI}$ , attributable to an inhomogeneity of the carrier concentration and to lattice deformation and/or defects.<sup>21,22</sup> As shown in the middle panels in Fig. 2, for single-element doping with Cr or Nb, the maximum TCR decreased monotonically with increasing dopant content, with Nb doping having the greater effect. In contrast to single-element doping, co-doped  $V_{0.95-x}Cr_xNb_{0.05}O_2$  films showed a nonmonotonic decrease with increasing  $x$ . The  $V_{0.95-x}Cr_xNb_{0.05}O_2$  films with  $x = 0.02, 0.05,$  and  $0.08$  had larger TCR values than that of the  $V_{0.95}Nb_{0.05}O_2$  film ( $x = 0$ ), as highlighted in the middle panel in Fig. 2(a). For  $x \geq 0.05$  ( $= y$ ), the  $x + y$  dependence of the TCR values for the  $V_{0.95-x}Cr_xNb_{0.05}O_2$  films is almost coincident with that for the  $V_{1-x}Cr_xO_2$  films. This behavior can be also seen in the  $V_{0.95-y}Cr_{0.05}Nb_yO_2$  films [the middle panel of Fig. 2(b)]. These results suggest that the presence of Cr dopant with the condition  $x \gtrsim y$  is essential for obtaining large TCR values in  $V_{1-x-y}Cr_xNb_yO_2$  films.

The bottom panels in Fig. 2 show that for single-element doping,  $\Delta T_{MI}$  also decreases monotonically with increasing dopant content and that it is reduced more efficiently by doping with Nb than with Cr. Note that the  $\Delta T_{MI}$  is defined as the difference in the temperatures at which a film has a given resistivity ( $\rho_{MI}$ ) during the heating and cooling phases. For this study, we choose  $\rho_{MI}$  as the value of  $\rho$  at the temperature of the TCR peak in the heating process.<sup>15</sup> In contrast to the TCR value, the  $x + y$  dependence of  $\Delta T_{MI}$  for both  $V_{0.95-x}Cr_xNb_{0.05}O_2$  and  $V_{0.95-y}Cr_{0.05}Nb_yO_2$  films

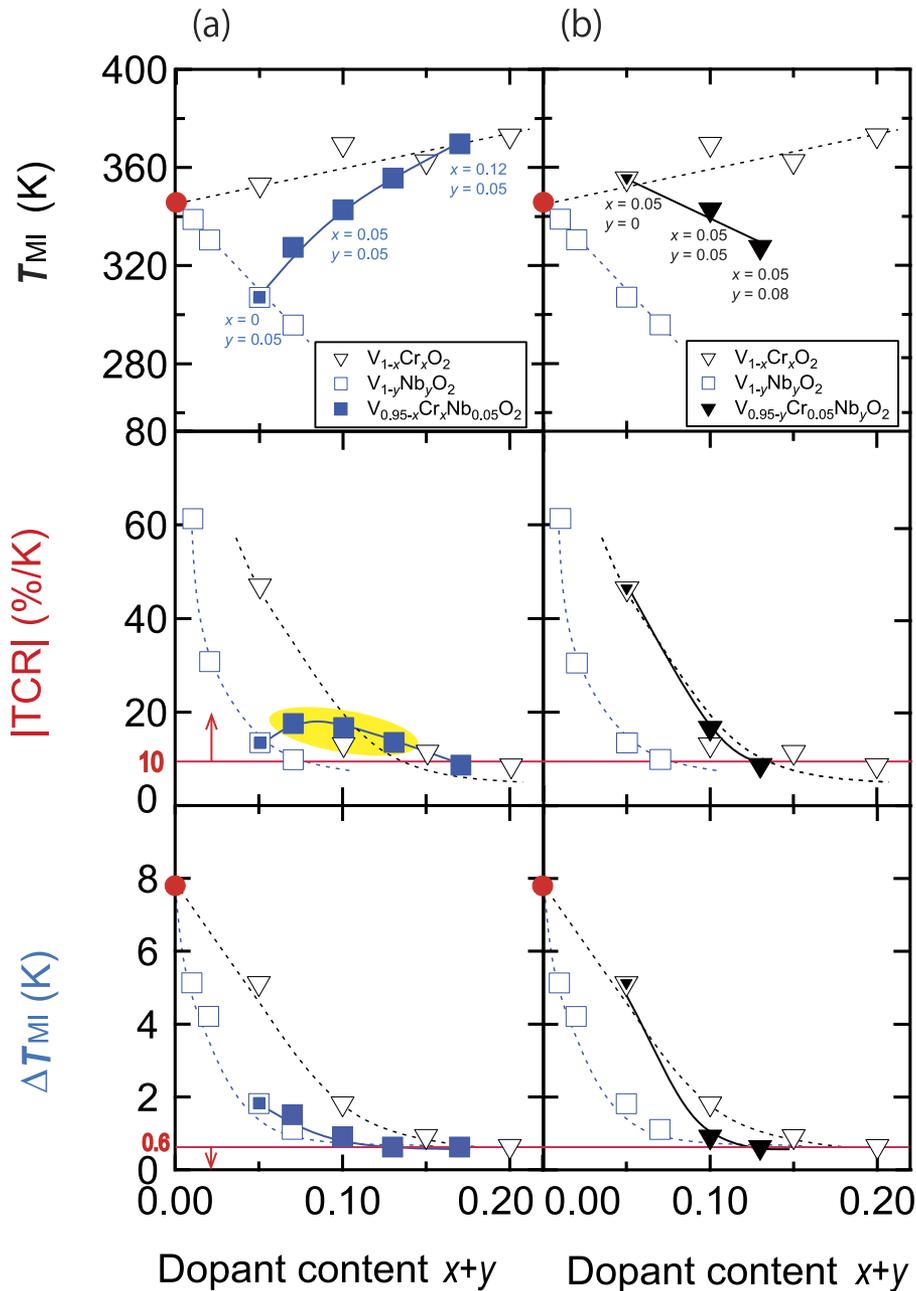


FIG. 2. Cr content ( $x$ ) and Nb content ( $y$ ) dependence of  $T_{MI}$ , TCR, and  $\Delta T_{MI}$  for (a)  $V_{0.95-x}Cr_xNb_{0.05}O_2$  and (b)  $V_{0.95-y}Cr_{0.05}Nb_yO_2$  films. An increase in the TCR in the  $V_{0.95-x}Cr_xNb_{0.05}O_2$  ( $x=0.02, 0.05$ , and  $0.08$ ) films with respect to that of the  $V_{0.95}Nb_{0.05}O_2$  ( $x=0$ ) film is highlighted.

approached that of  $V_{1-y}Nb_yO_2$  films. This result suggests that the presence of Nb dopant is essential for effectively reducing the  $\Delta T_{MI}$  with the minimum possible dopant content. Moreover, to realize a near absence of thermal hysteresis (defined as  $\Delta T_{MI} \leq 0.6$  K), a dopant content of  $x + y \geq 0.1$  is required.

We therefore found that co-doping of  $VO_2$  with Cr and Nb is an effective means of suppressing thermal hysteresis (i.e.,  $\Delta T_{MI}$ ) while retaining a large TCR. For  $V_{1-x-y}Cr_xNb_yO_2$  films, the conditions  $x \geq y$  and  $x + y \geq 0.1$  are essential for obtaining large TCR values in excess of 10%/K and a near absence of thermal hysteresis ( $\Delta T_{MI} \leq 0.6$  K), respectively. As seen in Fig. 2(a), large TCR values of 16.7%/K with a  $\Delta T_{MI} \approx 0.9$  K or 13.6%/K with  $\Delta T_{MI} \approx 0.6$  K were attained

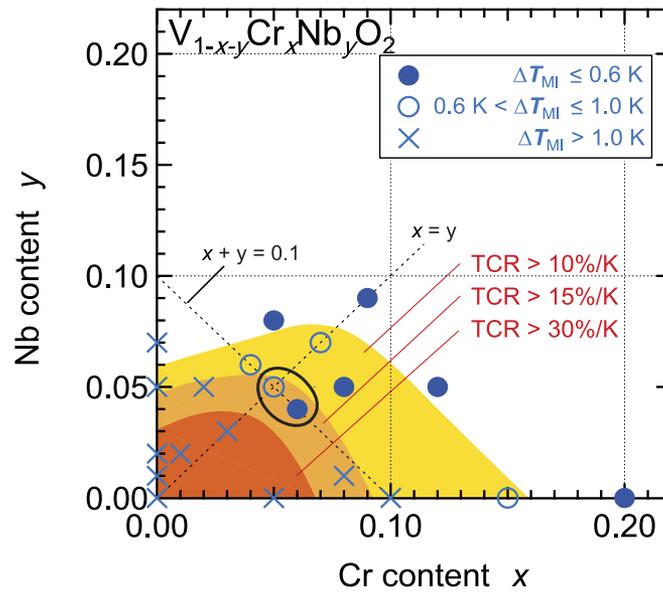


FIG. 3. TCR and  $\Delta T_{MI}$  diagram for  $V_{1-x-y}Cr_xNb_yO_2$  films as a function of the Cr and Nb contents. Values of  $\Delta T_{MI}$  are divided into three categories:  $\Delta T_{MI} \leq 0.6$  K (filled circles),  $0.6 \text{ K} < \Delta T_{MI} \leq 1.0$  K (open circles), and  $\Delta T_{MI} > 1.0$  K (crosses). The TCR values are classified into three regions:  $> 10\%/K$ ,  $> 15\%/K$ , and  $> 30\%/K$ .

with  $V_{0.90}Cr_{0.05}Nb_{0.05}O_2$  ( $x = 0.05$ ,  $y = 0.05$ ) and  $V_{0.87}Cr_{0.08}Nb_{0.05}O_2$  ( $x = 0.08$ ,  $y = 0.05$ ) films, respectively.

To further explore the optimal composition of the doped films, we examined the dependence of TCR and  $\Delta T_{MI}$  on  $x$  and  $y$  for  $V_{1-x-y}Cr_xNb_yO_2$  films on  $Al_2O_3$  substrates and we derived the diagram for the TCR and  $\Delta T_{MI}$  of the  $V_{1-x-y}Cr_xNb_yO_2$  films shown in Fig. 3. As  $x$  and  $y$  increase, the TCR value decreases monotonically. Relatively large TCR values were obtained near the line  $x = y$ . Furthermore, the TCR contour lines/domains are asymmetric with respect to this line. This asymmetry indicates that a condition of  $x \gtrsim y$  is suitable for obtaining a large TCR for  $V_{1-x-y}Cr_xNb_yO_2$  films, as mentioned earlier. In contrast to the TCR,  $\Delta T_{MI}$  does not show a clear trend with  $x$  and  $y$ . However, the diagram confirms that a practical absence of thermal hysteresis can be obtained for co-doped  $V_{1-x-y}Cr_xNb_yO_2$  films with  $x + y \geq 0.1$ . Therefore, because the total dopant content  $x + y$  should be as small as possible to obtain a large TCR, the optimal composition can be expected to be near the line  $x + y = 0.1$  with the condition  $x \gtrsim y$ , as shown by the solid circle in Fig. 3. In fact, among the films that showed practically no thermal hysteresis, the  $V_{0.90}Cr_{0.06}Nb_{0.04}O_2$  film showed the best TCR of 16.2%/K.

Next, we will briefly discuss the effects of Cr and Nb co-doping on the MIT of  $VO_2$ . One of the important effects of Cr and Nb co-doping is that of charge compensation. Because Cr and Nb ions are trivalent and pentavalent, respectively, Cr and Nb co-doping of  $VO_2$  has less overall effect on the change in the valence state of  $V^{4+}$  ions than does single-element doping. Therefore, any inhomogeneity of carrier concentration that results in a spatial variation in  $T_{MI}$  should be reduced in co-doped  $VO_2$  films. As a result, broadening of the MIT is suppressed, leading to an improvement in the TCR of the co-doped films. However, because of the different ionic radii of V, Cr, and Nb ions, Cr and Nb co-doping still induces lattice deformations and defects in  $VO_2$ . We previously reported that Cr doping suppresses the lattice changes in  $VO_2$  across the MIT that originate from a structural phase transition from a high-temperature tetragonal phase to a low-temperature monoclinic phase.<sup>15</sup> The suppression of this lattice change in the doped films might be the cause of the decrease in the TCR and  $\Delta T_{MI}$ . Because different doping elements induce different low-temperature monoclinic phases in  $VO_2$ ,<sup>18,19,23</sup> the lattice change across the MIT in the co-doped films is expected to be more complicated than that in the single-element doped films. To gain a better understanding of the effects of co-doping on the TCR and  $\Delta T_{MI}$ , detailed investigations of the structural properties of the co-doped  $VO_2$  films are required, and will be a subject of a further study.

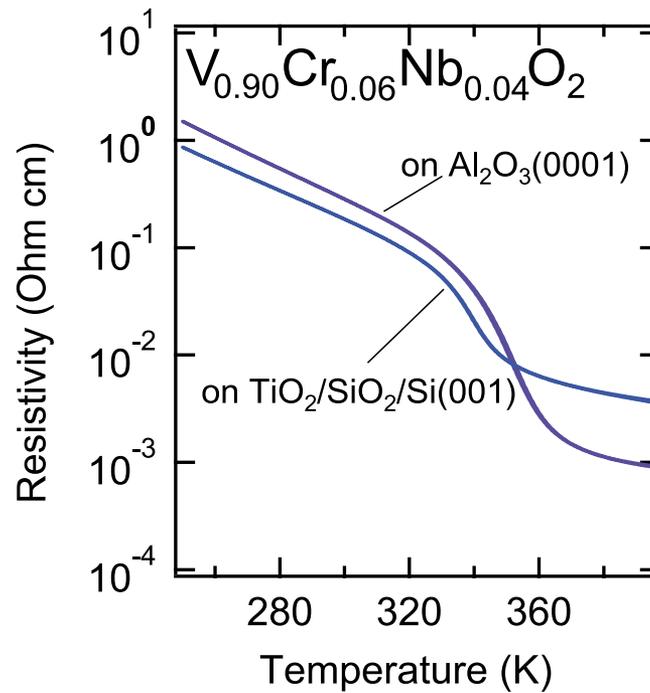


FIG. 4. Temperature dependence of the resistivity of  $V_{0.90}Cr_{0.06}Nb_{0.04}O_2$  films on  $Al_2O_3(0001)$  and  $TiO_2/SiO_2/Si(100)$  substrates.

For uncooled bolometer applications,  $VO_2$  films should be integrated onto Si platforms through a back-end-of-line (BEOL) process. We previously reported that  $TiO_2$  buffer layers permit the fabrication of  $VO_2$  films that show a sharp MIT on  $SiO_2/Si(100)$  substrates at process temperatures below 670 K, which is compatible with a BEOL process.<sup>17</sup> By using the  $TiO_2$ -buffer technique, we deposited  $V_{1-x-y}Cr_xNb_yO_2$  films on  $SiO_2/Si(100)$  substrates to realize both large TCR values and an absence of thermal hysteresis. Figure 4 shows the  $\rho$ - $T$  curves for the  $V_{0.90}Cr_{0.06}Nb_{0.04}O_2$  films on  $Al_2O_3$  and  $TiO_2/SiO_2/Si$  substrates. As mentioned earlier, the film on the  $Al_2O_3$  substrate showed practically no thermal hysteresis while retaining a large TCR of 16.2%/K. On the other hand, the film on the  $TiO_2/SiO_2/Si$  substrate showed a reduced  $\rho$  change across the MIT but retained a large TCR of 11.9%/K. This result suggests that a combination of co-doping and the  $TiO_2$ -buffer techniques provides an effective way of integrating a  $VO_2$  film having large TCR values and a practical absence of thermal hysteresis on a Si platform.

#### IV. SUMMARY

We have investigated the effects of co-doping of  $VO_2$  with Cr and Nb on the TCR and the thermal hysteresis of the MIT, and we have derived a TCR and  $\Delta T_{MI}$  diagram for  $V_{1-x-y}Cr_xNb_yO_2$  films on  $Al_2O_3$  substrates. The diagram showed that the doping conditions of  $x \gtrsim y$  (i.e., a slightly Cr-rich condition) and  $x + y \geq 0.1$  are suitable for simultaneously obtaining a large TCR and an absence of thermal hysteresis in the  $V_{1-x-y}Cr_xNb_yO_2$  films. By employing Cr and Nb co-doping and the  $TiO_2$ -buffer technique, we succeeded in obtaining a large TCR value of 11.9%/K with practically no thermal hysteresis in  $V_{0.90}Cr_{0.06}Nb_{0.04}O_2$  films deposited on  $SiO_2/Si$  substrates at process temperatures below 670 K, which are compatible with a BEOL process. This combined technique might be applicable in the development of  $VO_2$ -based uncooled bolometers with a high sensitivity.

<sup>1</sup> F. J. Morin, *Phys. Rev. Lett.* **3**, 34 (1959).

<sup>2</sup> J. B. Goodenough, *J. Solid State Chem.* **3**, 490 (1971).

<sup>3</sup> Z. Yang, C. Ko, and S. Ramanathan, *Annu. Rev. Mater. Res.* **41**, 337 (2011).

<sup>4</sup> M. Soltani, M. Chaker, E. Haddad, R. Kruzelecky, and J. Margot, *J. Vac. Sci. Technol. A* **25**, 971 (2007).

<sup>5</sup> S. Bonora, U. Bortolozzo, S. Residori, R. Balu, and P. V. Ashrit, *Opt. Lett.* **35**, 103 (2010).

- <sup>6</sup> Y. Gao, H. Luo, Z. Zhang, L. Kang, Z. Chen, J. Du, M. Kanehira, and C. Cao, *Nano Energy* **1**, 221 (2012).
- <sup>7</sup> R. Xie, C. T. Bui, B. Varghese, Q. Zhang, C. H. Sow, B. Li, and J. T. L. Thong, *Adv. Funct. Mater.* **21**, 1602 (2011).
- <sup>8</sup> M. Nakano, K. Shibuya, D. Okuyama, T. Hatano, S. Ono, M. Kawasaki, Y. Iwasa, and Y. Tokura, *Nature* **487**, 459 (2012).
- <sup>9</sup> H. Takami, K. Kawatani, T. Kanki, and H. Tanaka, *Jpn. J. Appl. Phys., Part 1* **50**, 055804 (2011).
- <sup>10</sup> S. Sedky, P. Fiorini, M. Caymax, A. Verbist, and C. Baert, *Sens. Actuators A* **66**, 193 (2003).
- <sup>11</sup> S. Eminoglu, D. S. Tezcan, M. Y. Tanrikulu, and T. Akin, *Sens. Actuators A* **109**, 102 (2003).
- <sup>12</sup> M. Moreno, A. Kosarev, A. Torres, and R. Ambrosio, *Thin Solid Films* **515**, 7607 (2007).
- <sup>13</sup> M. Nishikawa, T. Nakajima, T. Kumagai, T. Okutani, and T. Tsuchiya, *J. Ceram. Soc. Jpn.* **119**, 577 (2011).
- <sup>14</sup> I. Takahashi, M. Hibino, and T. Kudo, *Jpn. J. Appl. Phys., Part 1* **40**, 1391 (2004).
- <sup>15</sup> K. Miyazaki, K. Shibuya, M. Suzuki, H. Wado, and A. Sawa, *Jpn. J. Appl. Phys., Part 1* **53**, 071102 (2014).
- <sup>16</sup> M. Soltani, M. Chaker, E. Haddad, R. V. Krizelecky, and J. Margot, *Appl. Phys. Lett.* **85**, 1958 (2004).
- <sup>17</sup> K. Miyazaki, K. Shibuya, M. Suzuki, H. Wado, and A. Sawa, *J. Appl. Phys.* **118**, 055301 (2015).
- <sup>18</sup> J. P. Pouget and H. Launois, *J. Phys. Colloq.* **37**, C4-49 (1976).
- <sup>19</sup> G. Villeneuve, A. Bordet, A. Casalot, J. P. Pouget, H. Launois, and P. Lederer, *J. Phys. Chem. Solids* **33**, 1953 (1972).
- <sup>20</sup> M. Pan, H. M. Zhong, S. W. Wang, J. Liu, Z. F. Li, X. S. Chen, and W. Lu, *J. Cryst. Growth* **265**, 121 (2004).
- <sup>21</sup> A. Sharoni, J. G. Ramirez, and I. K. Schuller, *Phys. Rev. Lett.* **101**, 026404 (2008).
- <sup>22</sup> H. Takami, T. Kanki, and H. Tanaka, *Appl. Phys. Lett.* **104**, 023104 (2014).
- <sup>23</sup> J. B. Goodenough and H. Y.-P. Hong, *Phys. Rev. B* **8**, 1323 (1973).