

Anisotropic optical response of nanocrystalline V_2O_5 thin films and effects of oxygen vacancy formation

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We report a high sensitivity to oxygen vacancy formation as well as the temperature dependence of anisotropic optical properties of a nanocrystalline V_2O_5 thin film. Spectroscopic ellipsometry data show that the film has a uniaxial optical anisotropy due to a highly ordered nanocrystalline layer structure. The anisotropic optical properties of the film begin to change at ~ 400 K in a high vacuum and can be linked to the changes in the electronic structure of the film upon reduction. An increase in the refractive indices, anisotropic changes of the optical conductivities, and a decrease in film thickness are observed after vacuum heating and are recovered to original values by heating in air up to 480 K. The experimental results are supported by the previous theoretical studies on the stability of reduced V_2O_5 surface through the formation of oxygen vacancies. We discuss the formation of oxygen vacancies, vacancy-induced structural relaxations, and changes in the electronic structure of V_2O_5 in conjunction with the experimental results.

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I. INTRODUCTION

V_2O_5 (vanadium pentoxide), which has a layered crystalline structure with interlayer van der Waals interaction, is one of the most widely studied transition metal oxides because of its technological applications in Li-ion batteries [1], electrochromic devices [2], and a catalyst material in selective catalytic reduction units [3]. These interesting properties have been attributed to the ease of oxygen removal from the lattice of V_2O_5 [4,5]. In fact, oxygen vacancy in transition metal oxides has been an intensive research issue and plays an important role in determining the functional properties of oxides as well as surface properties [4]. Much research has focused on the changes in electronic structure by the formation of oxygen vacancies [4,6–10]. A reversible surface metal-insulator transition has been reported on a V_2O_5 (001) single crystal at 350–400 K by inducing oxygen vacancies in an ultrahigh vacuum [11]. In particular, the formation and dynamics of oxygen vacancies are critical issues in understanding the operation of emergent technological devices, such as solid oxide fuel cells [12] and electroresistive memories [13]. Despite the intensive efforts to investigate oxygen vacancies, there is still no full understanding of the formation of oxygen vacancy, especially oxygen vacancy-induced lattice relaxations, because of the experimental difficulties [14].

Interestingly, theoretical studies have found that structural relaxation in the V_2O_5 lattice is induced by the formation of oxygen vacancy and reduces the oxygen vacancy formation energy significantly, resulting in a distinct effect on the electronic structure of reduced surface [4,6–10]. The structural relaxation at the surface of the layered V_2O_5 structure upon reduction is of particular interest because the atomic displacement can be large enough to detect and cause significant changes in the functional properties [6,10]. However, an experimental

determination of the vacancy-induced lattice relaxations has been difficult, and the effects of oxygen vacancy formation on the physical properties of V_2O_5 have not been well studied since oxygen vacancy formation is limited only to the surface layer(s) even at high temperatures [11] and depends on supporting materials in thin films [15].

In this paper, we present our ellipsometric study of the effects of oxygen vacancy formation on the optical properties of V_2O_5 nanocrystalline film. The temperature dependence of the optical properties of the film is investigated in a high vacuum ($< 1 \times 10^{-6}$ Torr) in the temperature range of 300–480 K using spectroscopic ellipsometry (SE). A highly ordered layered nanostructure of the film gives rise to a uniaxial optical anisotropy that is effective in studying the surface-limited oxygen vacancy formation because of the high specific surface area. We find that the optical properties of the film are quite sensitive to oxygen vacancy formation. The temperature dependencies of SE data show that the anisotropic optical properties of the film begin to change at ~ 400 K in a high vacuum and are recovered to the original state by a reoxidation process. We discuss the anisotropic optical properties of the nanocrystalline V_2O_5 film, the structural relaxation associated with oxygen vacancy formation, and the changes in electronic structure upon reduction.

II. EXPERIMENTS

Nanocrystalline V_2O_5 films about 320 nm thick were prepared by a two-step process. First, highly (001) textured VO_2 films mixed with a V_2O_3 phase ($V_2O_{5-\delta}$, $1 \leq \delta \leq 2$) were grown on (0001) sapphire substrates at 673 K by aerosol-assisted chemical vapor deposition with the source solution made of vanadium acetylacetonate dissolved in 2-methoxyethanol. The nanocrystalline V_2O_5 films were then obtained by annealing the $V_2O_{5-\delta}$ films at 773 K for 30 min in oxygen. X-ray diffraction and high-resolution transmission

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electron microscopy (HRTEM) were used to ensure the nanostructure of the films. The SE measurements for the nanocrystalline V_2O_5 film were performed in a high vacuum ($< 1 \times 10^{-6}$ Torr) in the temperature range of 300–480 K by using a spectroscopic ellipsometer (VASE model, J. A. Woollam Co.) in the photon energy range of 0.7–5.2 eV at an incidence angle of 70° . In addition, for the original V_2O_5 film before the vacuum heating, SE measurements were carried out at three different incidence angles of 65° , 70° , and 75° to justify model fittings. A thermal equilibrium condition was maintained during the measurements: After reaching the desired temperature, we waited 10 min and carried out SE measurements for 60 min at each temperature. Compared to other optical spectroscopy techniques, such as reflectivity and transmittance measurements, SE is very sensitive to thin film, providing high accuracy and reproducibility because it measures information on both the intensity and the phase between two orthogonal linear polarization states of light [16]. Reoxidation of the films was carried out by heating the film to 480 K in air at the atmospheric pressure.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Amorphous V_2O_5 films have attracted much attention, especially for battery and electrochromic applications, because of their high capacity to intercalate larger amounts of lithium than the corresponding crystalline samples [17]. After annealing the $V_2O_{5-\delta}$ films at 773 K for 30 min in oxygen, the films became yellowish transparent, and no distinctive x-ray diffraction peak was observed, possibly indicating the formation of an amorphous V_2O_5 phase. However, the cross-sectional HRTEM image, as shown in Fig. 1, reveals that the amorphouslike V_2O_5 film has a highly ordered nanocrystalline structure. Ordered nanocrystalline layer structures with a typical size less than 5 nm are found in large parts of the cross-sectional

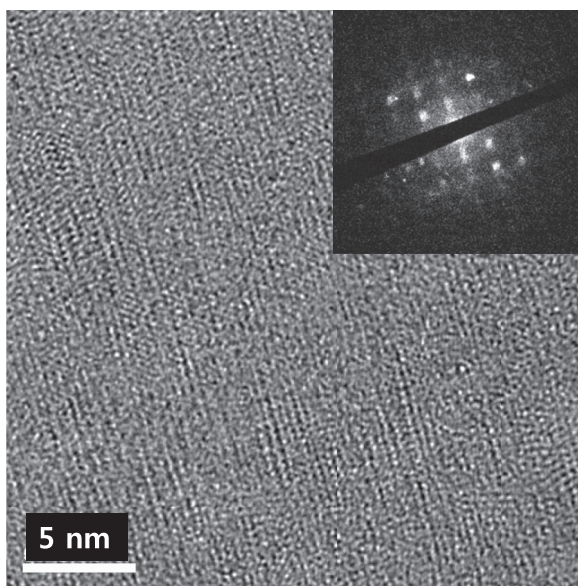


FIG. 1. Cross-sectional HRTEM image of the amorphouslike V_2O_5 film, showing a highly ordered nanocrystalline layer structure of the film. The inset is a selected area electron diffraction pattern.

HRTEM image. The weak and blurred diffraction spots in a selected area electron diffraction pattern (inset in Fig. 1) reveal the highly ordered nanostructure of the film. We also observed that oxygen annealing of $V_2O_{5-\delta}$ films at 823 K for 30 min resulted in a highly (001) textured V_2O_5 film with a large grain growth (not shown). To investigate the effects of oxygen vacancy formation, SE measurements were carried out for the amorphouslike nanocrystalline V_2O_5 films since oxygen removal from epitaxial V_2O_5 films supported on (0001) sapphire is difficult [15].

Figure 2(a) shows the pseudodielectric functions ($\langle \epsilon \rangle = \langle \epsilon_1 \rangle + i \langle \epsilon_2 \rangle$) of the nanocrystalline V_2O_5 film converted from the ellipsometric angles measured at room temperature for the original and vacuum-heated films. We notice that the pseudodielectric functions of the vacuum-heated film are different from the original one. The SE data were fitted with a three-layer model, including a surface roughness layer, the V_2O_5 film, and a sapphire substrate. The spectra show interference patterns below the fundamental optical band gap (~ 2.3 eV) of V_2O_5 , where the film is transparent, consistent

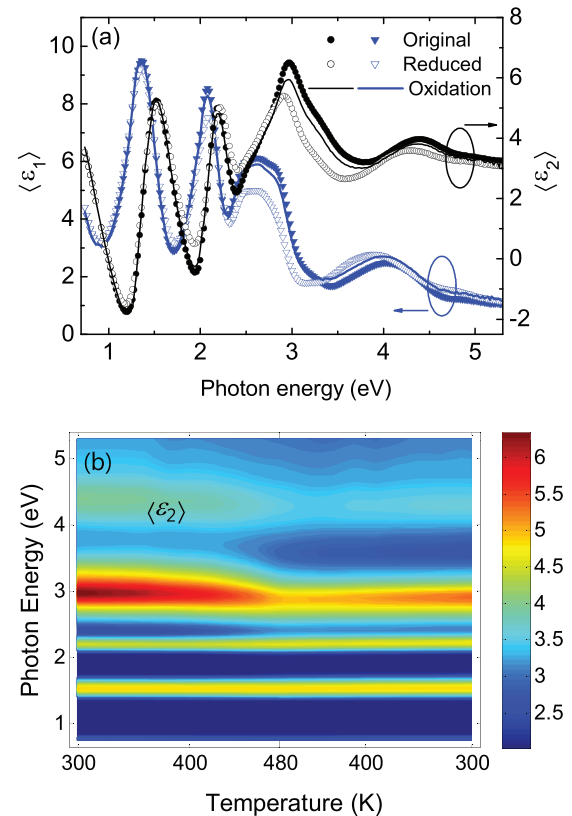


FIG. 2. (Color online) (a) Real (solid symbols) and imaginary (open symbols) parts of the pseudodielectric functions ($\langle \epsilon \rangle = \langle \epsilon_1 \rangle + i \langle \epsilon_2 \rangle$) of the nanocrystalline V_2O_5 film before and after heating to 480 K in a high vacuum. Mean squared error for the fit quality is obtained to be 0.322 for the pseudodielectric functions. The solid lines are the data for the reoxidized film heated to 480 K in air. The thickness of each layer is determined to be about 19 and 316 nm for the surface roughness layer and V_2O_5 film, respectively. (b) Intensity plot of the temperature dependence of $\langle \epsilon_2 \rangle$ obtained during high vacuum heating up to 480 K and the subsequent cooling processes, showing an irreversible change in the optical properties.

with a previous report [18]. Interestingly, the best fit of the experimental data is achieved by assuming that the film has a uniaxial anisotropy with the optical axis perpendicular to the surface of the film. The optical anisotropy of the film was confirmed by fitting additional SE data measured at different incidence angles of 65, 70, and 75° before vacuum heating. The highly ordered layer structure of the film may give rise to the uniaxial anisotropy of the nanocrystalline V_2O_5 film [18] since the optical property of layered V_2O_5 single crystal is highly anisotropic [19].

We observed that experimental data for ellipsometric angles changed significantly as the temperature of the nanocrystalline V_2O_5 film increases in a high vacuum. The overall temperature dependence of the pseudodielectric function is shown in Fig. 2(b) for the peak intensity of $\langle \epsilon_2 \rangle$, with an irreversible change in the optical properties of the film upon heating and subsequent cooling in a high vacuum. The differences in the optical properties are much clearer in the absorptive spectral range above 2.3 eV, where the electronic transitions from oxygen 2*p* levels to vanadium 3*d* levels are dominant in the vanadium octahedral structure [4]. The changes begin to occur at ~400 K during heating in a high vacuum and become significant above 420 K, probably due to the formation of appreciable amounts of oxygen vacancy. This behavior is in contrast to the case of single crystal, where thermally induced reduction is suggested to occur at 800 K [11]. It seems that the nanocrystalline structure of the V_2O_5 film is an important factor for observing the effects of oxygen vacancy formation. The anisotropic optical response is recovered nearly to the original state by heating the films in air up to 480 K several times, as indicated with solid lines in Fig. 2(a). This confirms that the redox reaction is responsible for the changes in the optical properties.

For further insight into the effects of oxygen vacancy formation on the anisotropic optical properties, the dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) of the nanocrystalline V_2O_5 film was modeled with four Gaussian oscillators in the whole spectral range. The Gaussian line shape resulted in a better fitting than the Lorentzian, probably due to the high defect density of the nanocrystalline film [20]. The surface roughness layer was modeled with the Bruggeman effective medium approximation by assuming a 50:50 ratio between void and V_2O_5 phase [18]. Figures 3(a) and 3(b) show the spectra of the refractive index (n) in the whole spectral range and transparent region, respectively, derived from the uniaxial anisotropy model analysis for the original and reduced states of the films at room temperature. The spectra at 480 K in a high vacuum are shown for comparison in dashed lines in Fig. 3(a). The spectra clearly show the strong optical anisotropy of the film for light propagating with the electric field vector parallel (ordinary n_o) and perpendicular (extraordinary n_e) to the film surface. The overall behavior is in good agreement with the results for V_2O_5 single crystal [19], if the ordinary part of the refractive index is considered as the average of the refractive indices for the crystallographic directions a and b of the orthorhombic V_2O_5 , where the V_2O_5 layer normal corresponds to the crystallographic direction c . Remarkably, the anisotropic optical properties of the films are quite sensitive to reduction: the refractive indices are increased by oxygen vacancy formation in the transparent region of the film below

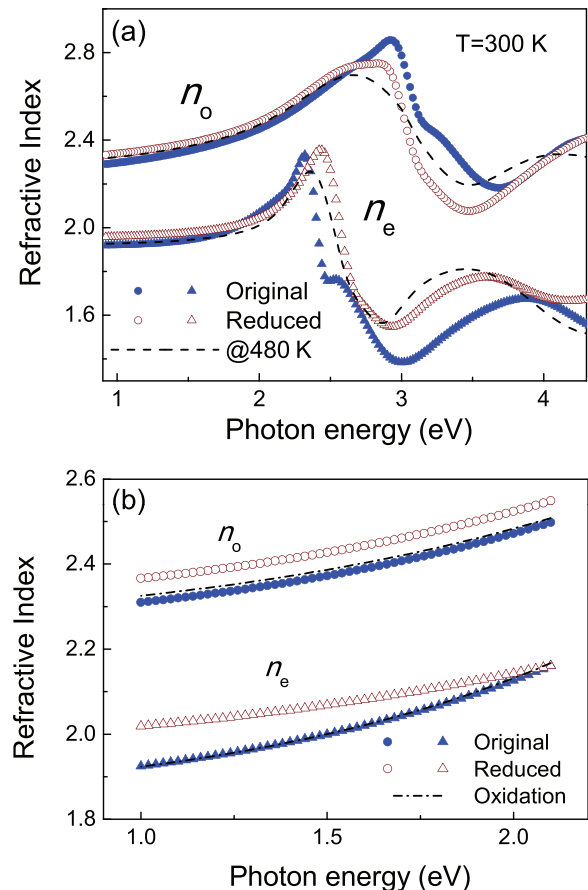


FIG. 3. (Color online) (a) Ordinary and extraordinary parts of the refractive index (n) in the whole spectral range before (solid symbols) and after reduction (open symbols). The spectra measured at 480 K in a high vacuum are shown with dashed lines for comparison. (b) Refractive indices in the transparent spectral region. The refractive indices after reoxidation process are also shown with dash-dotted lines.

~1.8 eV, as shown in Fig. 3(b). The increase in the refractive indices of the film may be due to oxygen vacancy-induced structural relaxation and/or charge carrier effects [21]. The refractive indices begin to recover their original values after heating the sample in air up to 480 K.

The most distinctive effect of reduction is anisotropic changes in optical conductivities. Figures 4(a) and 4(b) are the intensity plots of the optical conductivities as a function of temperature and photon energy for the ordinary and extraordinary parts, respectively. Optical conductivities for the original and reduced films measured at room temperature are also shown with those measured at 480 K for comparison. The optical conductivities for the ordinary part is about two to three times larger than those for the extraordinary part, in agreement with the theoretical calculation for single crystal [19]. It is interesting to note that changes in the anisotropic optical conductivities are also quite anisotropic upon reduction. For the ordinary part of the optical conductivities, the double-peak feature at the absorption edge changes to single peak above 400 K, while the extraordinary part preserves nearly the same double-peak feature up to 460 K in a high vacuum.

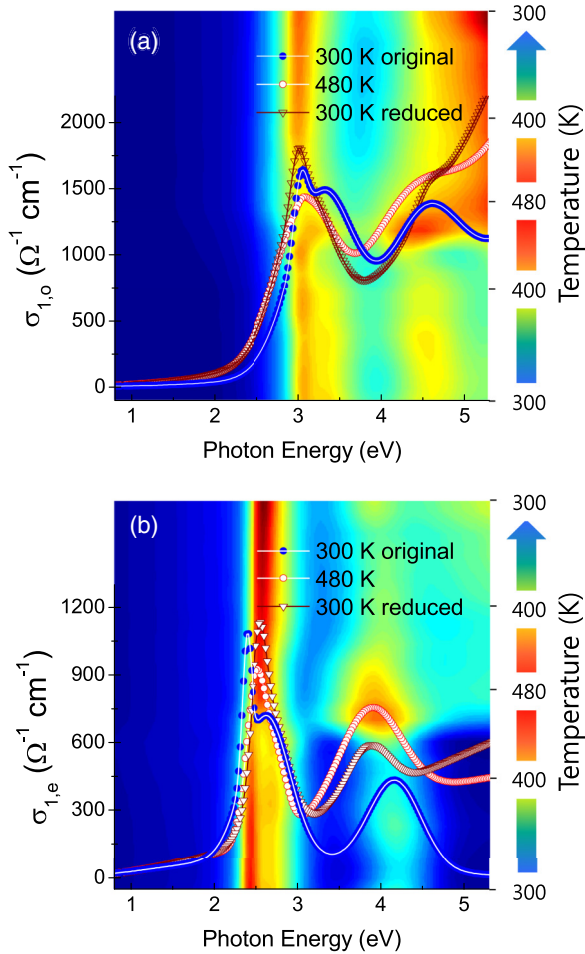


FIG. 4. (Color online) Intensity plots of the optical conductivity of the amorphouslike V_2O_5 film for (a) the ordinary and (b) extraordinary parts as a function of temperature and photon energy. Room-temperature optical conductivities for the original (solid circles) and reduced (reversed open triangles) films are shown with those at 480 K (open circles).

In addition, for the ordinary part of the optical conductivities, a significant change is observed at the higher energies above 4 eV upon reduction, as shown in Fig. 4(a). It is believed that the highly ordered nanostructure of the film and increase in oxygen vacancy leading to row formation on the V_2O_5 surface layer [4,6] should be responsible for the anisotropic changes in the optical conductivity. The excess electrons created by the formation of the oxygen vacancy, which are distributed over the closer V sites, change the band structure of the surface layers [10,11]. Also, oxygen vacancies on the surface layer may cause the formation of the V_6O_{13} or/and V_2O_3 phase at the surface of the nanocrystallites, without affecting much of its bulk properties [11]. These effects might be reflected mainly in the ordinary part of the optical conductivity. The metallic behavior observed at higher temperature around 550 K in polycrystalline V_2O_5 films may also be related to the formation of oxygen vacancies at the surfaces (grain boundaries) without a structural change [22]. These results might be related to changes in the electronic structure of V_2O_5 film by the formation of oxygen vacancy.

TABLE I. Resonance energies (E_n ; $n = 1, 2, 3, 4$) for the Gaussian oscillators used to model the nanocrystalline V_2O_5 film before and after vacuum heating to 480 K. (O) and (E) designate the values for ordinary and extraordinary parts, respectively. The values of E_4 for the extraordinary part were excluded because of large uncertainty.

	Oscillator resonance energy (eV)			
	E_1	E_2	E_3	E_4
Original film (O)	3.03 ± 0.02	3.25 ± 0.02	4.47 ± 0.07	14 ± 1
(E)	2.38 ± 0.02	2.59 ± 0.02	4.00 ± 0.05	–
Reduced film (O)	2.99 ± 0.02	3.03 ± 0.02	4.54 ± 0.07	8.9 ± 0.2
(E)	2.53 ± 0.02	2.65 ± 0.02	3.83 ± 0.05	–

As for the change in the electronic structure by oxygen vacancy formation, theoretical and experimental investigations have shown that the formation of oxygen vacancies in V_2O_5 induces a broadening of the conduction band and a decrease in the band gap [10,11]. We notice that the V_2O_5 single crystal has split-off conduction bands ~ 0.5 eV below the upper conduction band range [4,10,23]. Considering the band structure of the V_2O_5 single crystal, the doublet peaks at the absorption edge in the optical conductivities can be correlated with the optical transition from the valence band to the localized intermediate and upper conduction bands separated by ~ 0.5 eV [18]. The changes in the doublet peaks to single ones upon reduction may be due to the broadening of the band structure of V_2O_5 and disappearance of band splitting by the formation of oxygen vacancy, as predicted by theoretical works [6–10]. Intriguingly, the shifts of optical conductivity peaks upon reduction are opposite to each other for the ordinary and extraordinary parts, resulting in a slight decrease in the optical anisotropy. These interesting behaviors are also shown in Table I for the resonance energies of Gaussian oscillators used to model the V_2O_5 film before and after the vacuum heating. The lowest resonance energy E_1 of the oscillators is oppositely changing upon reduction for ordinary and extraordinary parts, and the energy difference becomes smaller. This may be related to changes in V $3d$ states due to excess electrons localized at the V sites and the formation of a oxygen vacancy-induced $V^{4+}-O-V^{4+}$ interlayer bond between the surface and layers underneath [4,6,10]. Since the singly coordinated terminal (vanadyl) oxygen on the surface of V_2O_5 is the most favorable vacancy site [4,6–10], the formation of vanadyl oxygen vacancy can induce structural relaxation through the formation of a $V^{4+}-O-V^{4+}$ interlayer bond between the layers. Structural relaxation on the surface of V_2O_5 due to the formation of oxygen vacancies has been studied by many theoretical works using density functional theory [4,6–10]. Such interlayer bond formation may destroy partly the quasi-two-dimensional nature [23] of V_2O_5 and consequently would reduce the anisotropy of the optical properties. The high sensitivity of the optical properties to oxygen vacancy formation can be characteristic of amorphouslike nanocrystalline films in which a large surface area of nanocrystallites may cause an increase in the number of oxygen vacancies and render the associated lattice relaxation more easily [4,6–10].

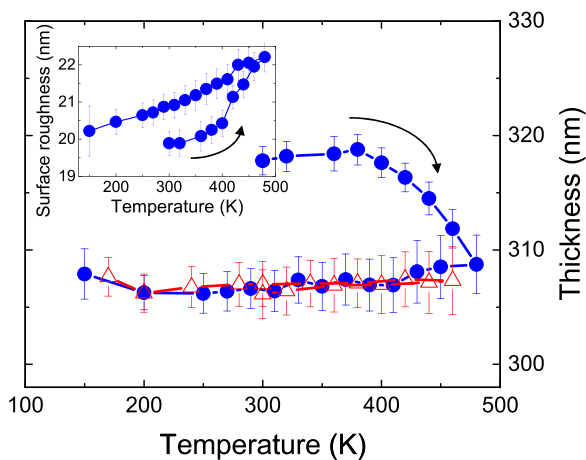


FIG. 5. (Color online) Change in film thickness during vacuum heating up to 480 K and the subsequent cooling to 150 K in a high vacuum (solid circles). The data were obtained from the model fittings of the SE data. Temperature dependence of film thickness after reduction (open triangles) was also measured during heating in a high vacuum. The inset shows the temperature dependence of surface roughness obtained from the same model fittings.

Finally, from the model fittings, the film thickness is found to decrease up to about 3% during the reduction process, as shown in Fig. 5. The film thickness begins to decrease at around 400 K in a high vacuum, consistent with the observed temperature dependence of the optical properties of the V_2O_5 film. The subsequent decrease (filled circles) and increase (open triangles) in temperature does not give rise to any significant change in film thickness. We believed that the decrease in the film thickness should be related to the structural relaxation of the V_2O_5 film due to the formation of oxygen vacancies. It has been found theoretically that the largest structural change associated with the formation of vanadyl oxygen vacancy is the decrease of the interlayer distance up to about 12%, with the interlayer $V^{4+}-O-V^{4+}$ bond formation between the surface and the beneath layers [4,6,10]. For a V_2O_5 single crystal, structural relaxation has been difficult to reveal directly since it is only limited to the surface layer [11]. However, for the highly ordered nanocrystalline film, there should be many surface layers to form vanadyl oxygen vacancies, and the effects of structural relaxation can be detectable. The increase in the surface roughness upon reduction, as shown in the inset of Fig. 5, suggests inhomogeneous

structural relaxation in the nanocrystalline V_2O_5 film due to inhomogeneous oxygen vacancy formation. The temperature dependence of the surface roughness after reduction may be related to the highly anisotropic thermal expansion coefficients of the V_2O_5 ; the thermal expansion coefficient along the crystallographic c axis is about 7 and 25 times larger than those along the a and b axes, respectively [24]. The formation of nanostrain due to the different thermal expansion in the nanocrystalline V_2O_5 film may cause temperature dependence of surface roughness.

IV. SUMMARY AND CONCLUSION

We have observed a high sensitivity of the anisotropic optical properties of a highly ordered nanocrystalline V_2O_5 thin film to oxygen vacancy formation by using SE. The highly ordered layered nanostructure of the film gives rise to uniaxial optical anisotropy, reflecting the anisotropic optical properties of the V_2O_5 single crystal and a high sensitivity to oxygen vacancy formation. The increase in the refractive indices, anisotropic changes in the optical conductivities, and the decrease in film thickness are discussed in conjunction with oxygen vacancy-induced structural relaxations and changes in electronic structure associated with oxygen vacancy formation. Changes in $V 3d$ states due to excess electrons localized at the V sites, which can lead to a broadening of the electronic band structure, should be responsible for the change of the optical properties. Highly anisotropic changes in the optical conductivities at the photon energies above 4 eV is believed to be related to the formation of vacancy rows on the surface layer of V_2O_5 nanocrystallites. The decrease in the film thickness upon reduction may have a direct correlation with the formation of oxygen vacancy-induced $V^{4+}-O-V^{4+}$ interlayer bonds between the surface and layers underneath. Such a high sensitivity of the optical properties of the nanocrystalline V_2O_5 thin films to oxygen vacancy can be used in the optical detection of a redox reaction. Also, the highly ordered nanocrystalline V_2O_5 films may have a structural advantage in a high capacity Li-ion battery application as well as in high-performance catalysts.

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