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ABSTRACT

We demonstrate the epitaxial growth of thin films by thermal laser evaporation. Epitaxial metal oxide films are grown by laser evaporating Ni, V, and Ru elemental sources in a variety of oxygen-ozone atmospheres on laser-heated oxide substrates. This results in NiO (111), VO₂ (M1) (020), and RuO₂ (110) epitaxial films on Al₂O₃ (0001) or MgO (100) substrates. The films show well-defined crystallographic orientation relationships with the substrates, as confirmed by in-plane and out-of-plane x-ray measurements. The results reveal the potential of thermal laser epitaxy for the epitaxial growth of ultrahigh-purity oxide heterostructures.

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1. INTRODUCTION

The new physics and technological applications possible with oxide-based heterostructures demand the synthesis of ultraclean oxide materials with well-controlled atomic structure and composition. Thermal laser evaporation is a new deposition technique that enables ultraclean oxide growth by thermally evaporating pure metal sources by laser-induced local heating in an oxidizing atmosphere.1–3

The advantages and potential of thermal laser evaporation have been demonstrated by forming ultraclean metal and semiconductor films from most of the nonradioactive elements in the periodic table under vacuum conditions1–2 and by synthesizing polycrystalline oxide thin films under oxygen/ozone atmospheres on unheated Si (100) substrates.3 These results clearly show that thermal laser evaporation has the potential to combine the advantages of molecular beam epitaxy (MBE), pulsed laser deposition, and electron-beam evaporation, while avoiding their respective drawbacks. Thermal laser evaporation allows the use of ultrapure solid or liquid elements as source materials and controlling their molecular fluxes in a simple and precise way via laser irradiation. The simple configuration with all the power sources placed outside the growth chamber allows reactive gaseous constituents as source materials and a total pressure of up to 10⁻¹ hPa. In addition, it can guarantee the high purity of the grown thin films by preventing impurities from being incorporated into the sources because most solid sources can support themselves as their own crucibles due to a large temperature gradient by focused laser heating combined with efficient thermal losses due to black-body radiation in thermal laser evaporation. However, although the growth of a large variety of metal and oxide films has been demonstrated, epitaxial growth has not yet been achieved by thermal laser evaporation.

The epitaxial growth of oxide thin films is essential for fully exploiting the intriguing properties of oxide materials, in particular, those of oxide heterostructures. Oxide heterointerfaces can lead to new and unexpected effects.4–7 Although thermal laser evaporation has proven to be advantageous for growing oxide films, the epitaxy by thermal laser evaporation (called thermal laser epitaxy, TLE) of oxides using pure metal sources in oxidizing atmosphere needs to be demonstrated. It is imperative to address oxide TLE, bringing into effect the advantages of thermal laser evaporation.

In this study, we have performed TLE of pure metal sources in a variety of oxidizing atmospheres on laser-heated oxide substrates to find the process windows for oxide TLE. We readily succeeded in the epitaxial growth of three oxide thin films: NiO (111) on Al₂O₃ (0001), VO₂ (020) on Al₂O₃ (0001), and RuO₂ (110) on MgO (100). The epitaxial oxide films show clear crystallographic orientation relationships with the substrates. Our results reveal that TLE has great potential for the epitaxial growth of metal oxide thin films.
II. EXPERIMENT

The chamber for oxide TLE is schematically shown in Fig. 1. We used two fiber infrared (IR) lasers (1070 nm) placed outside the chamber to heat high-purity metal sources and oxide substrates, respectively. Optical ports have been used over a time span of more than a year without significant IR transparency drop by the deposited materials. The source and the substrate were each supported by Ta-based holders separated by a 60-mm working distance. The source-heating laser was focused on the source surface within an elliptical area of $\sim 1$ mm$^2$. A type C W-Re thermocouple was positioned at the bottom of the source to monitor the source temperature. The substrate was irradiated by applying a heating laser on its backside with a wide beam profile for more uniform heating. For IR-transparent oxide substrates, a 200-nm-thick Pt layer was sputtered onto the backside as a laser light-absorbing and heat-spreading layer. Before being loaded into the chamber, the substrates were cleaned by sonication in acetone and isopropyl alcohol and rinsed with distilled water. No additional substrate treatment was performed. The surface temperature of the substrates was measured by a pyrometer.$^8$

Figure 2 shows the surface temperature of a $10 \times 10 \times 1$ mm$^3$ Al$_2$O$_3$ substrate heated on its backside by IR laser irradiation with Pt metallization. We corrected the temperature deviation caused by the IR absorption of the window glass. The measured temperature values represent a lower bound of the actual surface temperature because the emissivity was set to unity. The inset of Fig. 2 shows an optical image of the Al$_2$O$_3$ substrate backside with the Pt layer heated by 100 W laser radiation. Although the limited beam size and the Gaussian beam profile introduce a temperature gradient toward the edges, the substrate center is rather uniformly heated within an area $\sim 4$ mm in diameter. Film analysis was performed only at the substrate center considering the heating characteristics.

An oxygen/ozone gas mixture was introduced into the chamber for oxide epitaxy. An ozone generator converted part of the 6 N oxygen gas into ozone. Ozone accounted for $\sim 10$ wt. % of the total gas flow. The oxidizing gas partial pressure ($P_{ox}$) was controlled within a range of $10^{-5}$ to $10^{-2}$ hPa by adjusting the gas inlet flow and the pumping speed. $P_{ox}$ affects the source flux by oxidizing the metal source$^3$ and by reducing the mean free path of the source vapor.$^7$ Considering a 60-mm working distance, the source flux at the substrate surface is expected to decrease if $P_{ox} > 10^{-3}$ hPa. However, we observe no drop of the growth rates even for $P_{ox} = 10^{-2}$ hPa, the highest pressure we have examined.$^3$

Cylindrical, high-purity metal sources were used: Ni (12 mm diameter), V (5 mm diameter), and Ru (6 mm diameter). The source size affects the laser power required for evaporation at a given rate. Smaller sources require less power for the same evaporation rate.$^2$ Al$_2$O$_3$ (0001) substrates were used for the TLE of Ni and V, and MgO (100) substrates were used for the TLE of Ru.

The oxide films were characterized by an in-house x-ray diffractometer with a Cu K-\(\alpha\) source. The preferred orientation of each oxide film and its in-plane orientation relationships with the substrate were determined by omega (\(\omega\))-2theta (2\(\theta\)) and phi (\(\phi\)) scans, respectively. Raman spectra of the VO$_2$ thin film were measured using a 633-nm laser to identify the crystal phase. Scanning electron microscopy (SEM) was performed to study the surface morphology of the oxide films.

III. RESULTS AND DISCUSSION

A. Epitaxial growth of cubic rock salt NiO on Al$_2$O$_3$ (0001)

We performed TLE of Ni in a $P_{ox}$ of $10^{-5}$ and $10^{-4}$ hPa on heated Al$_2$O$_3$ (0001) substrates. Figure 3 shows the x-ray diffraction (XRD) patterns of NiO films grown under various conditions. The NiO-I and II films were grown at $10^{-3}$ hPa with 500 and
700 °C substrate temperatures, respectively. The NiO-III and IV films were grown at 10^{-4} hPa with 500 and 700 °C substrate temperatures, respectively. The NiO films grown at 10^{-5} hPa (NiO-I and II) contain Ni phases, as shown by Fig. 3(a), which is consistent with the previous results of thermal laser evaporation of Ni at 10^{-5} hPa on unheated Si (100) substrates.3 The diffraction peak at around 44.5° is attributed to the Ni (111) reflection [marked by solid circles in Fig. 3(a)]. The relatively weaker Ni (111) reflection of NiO-II as compared to that of NiO-I indicates that the oxidation may be facilitated by the higher substrate temperature, instead of the expected reduction for higher temperature at \( P_{\text{ox}} = 10^{-5} \text{ hPa} \). The diffraction peaks close to 37.4° and 79.6° originate from the NiO (111) and NiO (222) reflections, respectively. Both the Ni and the NiO phases are expected to be (111)-oriented. The Ni phase disappears in the NiO films grown in a more strongly oxidizing atmosphere, and only the NiO phase is detected with a (111) orientation.
preferred orientation as shown in Fig. 3(b). Higher $P_{ox}$ and substrate temperature are, therefore, preferable for synthesizing NiO films within the tested growth conditions.

The NiO phases in both NiO-I and NiO-IV films exhibit an epitaxial relation with the Al$_2$O$_3$ (0001) substrate. The XRD $\varphi$ scans shown in Figs. 3(c) and 3(d) display the corresponding NiO (202) Bragg reflection versus the Al$_2$O$_3$ (116) Bragg reflection. The cubic rock salt NiO (202) Bragg reflection has a threefold symmetry. Therefore, the observed sixfold symmetry of the NiO (202) reflection indicates that the NiO (111) film has two domains rotated 180° to each other. The clear epitaxial relation between the NiO films and the Al$_2$O$_3$ substrate confirm that the NiO films grown by TLE from a pure Ni source are epitaxial.

The Ni metal phase observed in the NiO-I film, marked by the dot in Fig. 3(a), also has an epitaxial orientation with respect to both the NiO phase and Al$_2$O$_3$ substrate, as confirmed in Fig. 3(c) by an XRD $\varphi$ scan of the (202) Bragg reflection of cubic Ni. This implies that TLE is also applicable for metal thin film epitaxy. Analogous to NiO, the Ni phase is also composed of two domains with a 180° rotation relationship. The Ni domains are rotated 30° with respect to the NiO domains.

**B. Epitaxial growth of monoclinic VO$_2$ on Al$_2$O$_3$ (0001)**

Epitaxial monoclinic VO$_2$ thin films were grown by TLE of V at a $P_{ox}$ of $10^{-3}$ hPa on an Al$_2$O$_3$ (0001) substrate heated to 600 °C. Figure 4(a) displays the XRD $\omega$-$2\theta$ scan of the grown film. The peaks at 39.9° and 86.0° can be assigned to the (020) and (040) reflections of monoclinic VO$_2$, respectively. To determine unambiguously the phase of the grown VO$_2$ film among the possible vanadium oxides and their phases, Raman spectroscopy was conducted with a 633-nm laser as shown in Fig. 4(b). The Raman spectrum reveals the spectral signatures of the VO$_2$ (M1) structure, for example, $A_g$ phonons at 199, 226, 308, 381, 500, and 625 cm$^{-1}$, and $B_g$ phonons at 145, 226, 266, 391, 445, 580, and 826 cm$^{-1}$. Therefore, the grown film is found to be VO$_2$ (M1) with a (020) preferred orientation.

The epitaxial relation of the VO$_2$ (M1) films was clarified by XRD $\varphi$ scans such as the one shown in Fig. 4(c), which suggests an epitaxial alignment between the VO$_2$ film and the Al$_2$O$_3$ substrate according to VO$_2$ (M1) [100] || Al$_2$O$_3$ [1010]. As the (011) VO$_2$ (M1) Bragg reflection has a twofold symmetry, the sixfold symmetry of the (011) VO$_2$ (M1) $\varphi$ scan indicates the presence of three equivalent domains rotated 120° to each other. This agrees with the hexagonal symmetry of Al$_2$O$_3$ with three equivalent crystallographic directions and the monoclinic structure of VO$_2$ with a $\beta$ angle of ~122.6° between the $a$- and $c$-axes.

The $\beta$ angle of VO$_2$ (122.6°) produces a deviation in the epitaxial relationship between the $c$ axis of VO$_2$ and the [1100] axis of Al$_2$O$_3$, which may result in the evolution of multiple subdomains. We indeed observe multiple subdomains in VO$_2$ (M1) thin films deposited at higher substrate temperatures. The VO$_2$ film grown at a $P_{ox}$ of $10^{-3}$ hPa on Al$_2$O$_3$ (0001) at 680°C shows two subdomains rotated ~4.5° to each other. This is consistent with the $\beta$ angle of VO$_2$ (M1). Details of the VO$_2$ (M1) thin film with multiple subdomains are provided in the supplementary material.
Vanadium is a multivalent transition metal that can form a variety of oxides including $\text{V}_2\text{O}_3$, $\text{VO}_2$, and $\text{V}_2\text{O}_5$. We succeeded in forming three different vanadium oxides on an unheated Si (100) substrate dependent on $P_{\text{ox}}$. Correspondingly, we observed an epitaxial corundum structure of $\text{V}_2\text{O}_3$ domains on $\text{Al}_2\text{O}_3$ (0001) in a film grown in a less oxidizing atmosphere ($P_{\text{ox}}$ of $10^{-4}$ hPa) at 950 °C. XRD scans reveal an epitaxial relation of $\text{V}_2\text{O}_3$ (001) || $\text{Al}_2\text{O}_3$ (0001) and $\text{V}_2\text{O}_3$ [100] || $\text{Al}_2\text{O}_3$ [2100]. Triangular domains of epitaxially grown $\text{V}_2\text{O}_3$ are clearly observed with SEM. The trends found for the influence of the deposition conditions on the $\text{VO}_2$ and $\text{V}_2\text{O}_3$ formation are consistent with the phase diagram of the vanadium-oxygen system.

C. Epitaxial growth of RuO$_2$ on MgO (100)

RuO$_2$ is important for various device applications due to its appealing properties such as low resistivity at room temperature, high work function, and good thermal and chemical stability. In addition, interesting complex oxides with ruthenium, in particular, layered ruthenates and their intriguing properties, demand the growth of high-quality ruthenium oxide. MBE is one of the most advanced techniques for synthesizing such high-quality oxide thin films. However, it is challenging to synthesize ruthenium oxide by MBE because of the extremely low vapor pressure and the high oxidation potential of Ru requiring e-beam evaporation and simultaneously high oxygen partial pressures.

Despite using the same deposition physics as MBE, TLE has a particular strength in evaporating refractory metals including Ru. Local laser irradiation can readily evaporate refractory metals even above the melting point, and the absence of filament heaters in the chamber allows high oxygen/ozone partial pressures for complete oxidation. Using these advantages, we performed TLE of Ru on MgO (100) substrate under various conditions.

Figure 5(a) shows the XRD $\omega$-2θ pattern of a Ru (oxide) film deposited at a $P_{\text{ox}}$ of $10^{-4}$ hPa on MgO (100) at 500 °C substrate temperature. The diffraction peaks at around 27.9°, 57.8°, and 93.0° can be assigned to the (110), (220), and (330) planes of rutile RuO$_2$, respectively. This indicates that we have succeeded in using TLE to synthesize an RuO$_2$ thin film with a (110) preferred orientation.

The epitaxial relation between RuO$_2$ and MgO (100) substrates is determined to be RuO$_2$ (110) || MgO (100) and RuO$_2$ [001] || MgO [011] by an XRD $\varphi$ scan as shown in Fig. 5(b). The fourfold symmetry of the (200) Bragg reflection is attributed to two equivalent domains rotated 90° to each other. This is consistent with the surface morphology of the RuO$_2$ film [Fig. 5(c)] showing rectangular grains rotated 90° to each other.

In the other deposition tests, polycrystalline RuO$_2$ films or Ru-RuO$_2$ mixtures were obtained. Ru (oxide) films grown under weaker oxidation conditions ($P_{\text{ox}} = 10^{-5}$ hPa) at 500 °C MgO (100) contain crystalline metallic Ru together with RuO$_2$. Interestingly, rectangularly arranged grains are still observed on the surface. Under strongly oxidizing conditions ($P_{\text{ox}} = 10^{-3}$ and $10^{-2}$ hPa), no films were formed at substrate temperatures of 500 °C. We ascribe this to the formation of volatile ruthenium oxides such as RuO$_3$ or RuO$_4$ that readily desorb from the substrate surface. Without substrate heating, polycrystalline RuO$_2$ formed on the substrate. XRD

![FIG. 5.](image-url) Thermal laser epitaxy of RuO$_2$ on MgO (100). (a) XRD $\omega$-2θ patterns of a TLE-grown RuO$_2$ film. (b) XRD $\varphi$ scans for the RuO$_2$ (200) and MgO (220) Bragg reflections. (c) SEM image of the same RuO$_2$ epitaxial film.
patterns and surface morphologies of the polycrystalline RuO_2 films are collected in the supplementary material. As soon as the MgO (100) substrate is heated to 700 °C, the metallic Ru phase becomes dominant in the film. Figure S3.3 in the supplementary material shows XRD patterns of an Ru (oxide) film deposited at a P_{ox} of 10^{-4} hPa with 700 °C substrate temperature. In this film, rectangular domains are no longer observed.

**IV. SUMMARY AND CONCLUSION**

We have demonstrated TLE of three oxide film/substrate combinations: NiO (111) on Al_2O_3 (0001), VO_2 (M1) (020) on Al_2O_3 (0001), and RuO_2 (110) on MgO (100). The oxide epitaxial films were synthesized by TLE of pure metal sources on laser-heated substrates in an oxidizing atmosphere. The epitaxial relationships of the films and the substrates were determined by XRD ω-2θ and ϕ scans. The P_{ox} and the substrate temperature are found to determine the degree of oxidation of the grown films. Our results demonstrate the advantage of TLE in handling refractory metal sources for oxide film growth and open up new possibilities for the epitaxial growth of ultrahigh-purity oxide heterostructures.

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**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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