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Development of novel oxide multilayer mirrors at "water-window" wavelengths by atomic layer deposition / atomic layer epitaxy

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The authors proposed that novel oxide superlattice structures of crystalline TiO_2/ZnO on sapphire substrates could be fabricated for high-reflection multilayer mirrors at 2.734 nm. In the experimental study, both rutile TiO_2 (200) and wurtzite ZnO (0001) thin films were grown epitaxially on the same sapphire (0001) substrates by atomic layer epitaxy (ALE) at 450°C. the authors also demonstrated for the first time that the novel oxide superlattice structure of 10-bilayer TiO_2/ZnO on a sapphire substrate gave high reflectance at 2.734 nm.

Key words: soft x ray, water window, multilayer, ALD, ALE

1. INTRODUCTION

Since Barbee et al. successfully demonstrated near-normal-incidence (θ =15.5°) soft-x-ray reflectors with high reflectances of 67% at 17.0 nm using 20-bilayer Mo/Si multilayers deposited by magnetron sputtering [1], there have been various studies on the fabrication of soft-x-ray multilayer reflectors using electron beam evaporation and ion beam, rf and dc magnetron sputtering deposition. In particular, development of high-performance normal-incidence multilayer optics for the water-window wavelength region between the oxygen and carbon K absorption edges at 2.33 and 4.36 nm, respectively, where water is relatively transmissive and organic materials are absorptive, has been a technical challenge of great interest. The extremely small periods (1.2-2.2 nm) of soft-x-ray reflectors require very rigorous specifications to be met with respect to interface roughness and interlayer mixing, because interface roughness on an atomic scale has a substantial effect on soft-x-ray reflectance.

Although the Fresnel coefficients of materials are so small at these wavelengths that a large number of bilayers must be used, which means that the problems of interface roughness and imperfect interfaces due to interlayer mixing become serious, the highest reflectance achieved at water-window wavelengths (3.11 nm) and near normal incidence (θ=9.2°) has been reported to be 32% [2], owing to the various efforts which have been made in this field.

The authors have proposed the use of a novel metal oxide multilayer for soft-x-ray reflectors at water-window wavelengths [3], because an oxide multilayer can prevent the formation of an alloy at the interface, and the absorption of oxygen in oxides is negligible at the water-window wavelengths; moreover, the metal oxide multilayer can be fabricated by the atomic layer deposition or atomic layer epitaxy technique. These techniques can be used to control surfaces on an atomic scale by sequentially dosing the surface with appropriate chemical precursors and then promoting surface chemical reactions which are inherently self-limiting. We have found that the self-limiting adsorption mechanism works in the fabrication of oxide thin films such as aluminum oxide and titanium oxide [4-7]. And we reported that we have experimentally demonstrated high reflectance of over 30% at a wavelength of 2.734 nm and an incident angle of 71.8° from the normal incidence using novel metal oxide multilayers of titanium oxide and aluminum oxide fabricated by the atomic layer deposition method of controlled growth with sequential surface chemical reactions. For x-ray processing, crystalline multilayer mirrors might be rather useful than amorphous ones. Therefore, the authors demonstrated that novel oxide superlattice structures of crystalline TiO_2/ZnO on sapphire substrates were fabricated for high-reflection multilayer mirrors at 2.734 nm recently.

2. EXPERIMENTAL SETUP

The schematic diagram of the experimental set-up is presented in Fig. 1. It is comprised of a stainless-steel vacuum chamber, three computer–controlled leak valves, a turbo molecular pump (TMP), a capacitor manometer, a cold cathode gauge, and an infrared-ray heater.

The vacuum chamber was evacuated by a TMP and the pressure in the chamber during the deposition was maintained below 10^{-6} Torr. The substrate temperature was 450 °C. Reactant vapors were introduced alternately through three computer-controlled leak valves.

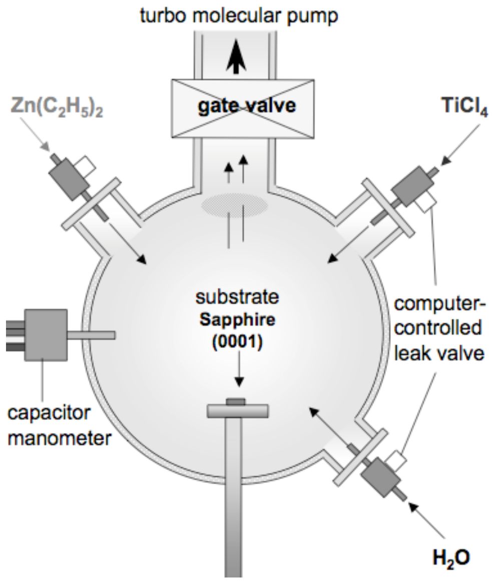

Fig. 1 Schematic diagram of apparatus.

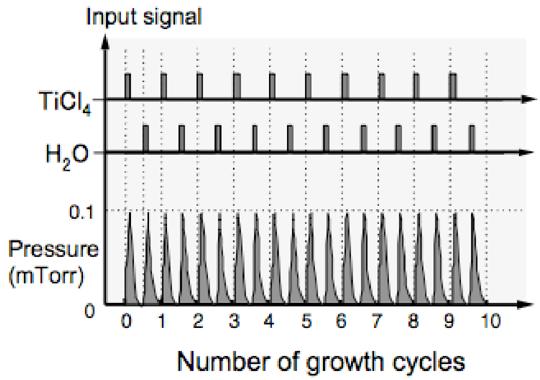

Fig. 2 Schematic diagram of input signals applied on the computer controlled leak valves.

As a substrate, sapphire (0001) was used. To obtain clean surface, the substrate was ultrasonically cleaned in acetone. ZnO films were deposited using diethylzinc (DEZ) as a source of Zn, water (H_2O) as a source of oxygen, while TiO_2 films were deposited using tetrachlorotitanium (TCT) as a source of Ti, water (H_2O) as a source of oxygen. The deposition cycle process consisted of repeated cycles, which contained 1 s dosing of DEZ (TCT), 2 s evacuation, 1 s dosing of H_2O, and 2 s evacuation. One growth cycle takes 6 s. Figure 2 shows DEZ and H_2O input signals applied to computer-controlled leak valves and they supply the pressure pulses of reactant vapor in the growth chamber.

The film thickness and refractive index of the ZnO and TiO_2 single layer films were determined using a variable angle spectroscopic ellipsometer. The crystallinity was measured using x-ray diffraction analysis (XRD) (Cu-Kα), and the multilayer periodicity was examined by using low-angle XRD. The reflectivity for soft x-rays was measured using monochromatized synchrotron radiation (SR) located Ultraviolet Synchrotron Radiation Facility (UVSOR), Institute for Molecular Science, Okazaki, Japan.

3. ATOMIC LAYER EPITAXY OF ZnO AND TiO_2 FILMS ON SAPPHIRE SUBSTRATE

First of all, we investigated the self-limiting condition with varying reactant vapor pressures. Figure 3 shows plots of the growth rate of ZnO films on sapphire (0001) as a function of the vapor pressures of DEZ and H_2O. Growth rates were determined from the thickness of the film divided by the number of growth cycles. Here, the number of growth cycle was 90 and deposition temperature was 450°C. As shown in Fig. 3, the growth rate of ZnO was found to be near 0.26 nm/cycle when the vapor pressures of DEZ and H_2O are between $3x10^{-4}$ Torr and $7x10^{-4}$ Torr. It is noteworthy the length of ZnO (0001) monolayer. Moreover, the refractive indices (λ =632.8 nm) of ZnO films were about 1.92 from $3x10^{-4}$ Torr to $7x10^{-4}$ Torr. This value of 1.92 is close to the index of refraction of a ZnO bulk crystal [8]. These results indicate that self-limiting window is observed in the vapor pressure ranging from $3x10^{-4}$ Torr to $7x10^{-4}$ Torr. The film thickness of ZnO on sapphire (0001) increased with increasing the cycle number, when the deposition temperature was 450 °C and the vapor pressures of DEZ and H_2O were $4x10^{-4}$ Torr. The growth rate was constant as 0.26 nm/cycle. This result indicates that ZnO film thickness can be controlled by the number of cycle. Figure 4 shows the results of XRD measurements of ZnO film prepared 90 cycles at 450 °C. Both the wurtzite (0002) reflection peak is observed.

Figure 5 also shows plots of the growth rate of TiO_2 films on sapphire (0001) as a function of the vapor pressures of TCT and H_2O. Here, the number of growth cycle was 180 and deposition temperature was 450 °C. As shown in Fig. 5, the growth rate of TiO_2 was found to be near 0.076 nm/cycle, when the vapor pressures of TCT and H_2O are between $3x10^{-4}$ Torr and $6x10^{-4}$ Torr. The growth rate of 0.076 is nearly one-third the length of rutile (200) monolayer [9]. This indicates that self-limiting window is observed in the vapor pressure range from $3x10^{-4}$ Torr to $6x10^{-4}$ Torr.

The film thickness of TiO_2 on sapphire (0001) increased with increasing the cycle number, when the deposition temperature was 450 °C and the vapor pressures of TCT and H_2O were $5x10^{-4}$ Torr. The growth rate was constant as 0.076 nm/cycle, indicating that TiO_2 film thickness can also be controlled by the number of cycle.

Figure 6 shows the results of XRD measurements of TiO_2 film prepared 180 cycles at 450 °C. An intense rutile (200) peak is observed. This result indicates that TiO_2 film is grown on sapphire (0001) substrate epitaxially.

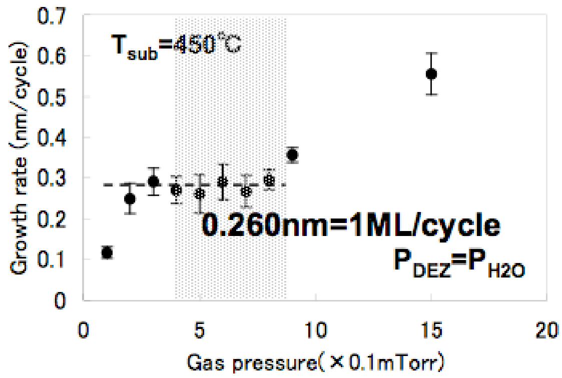

Fig. 3 Growth rate of ZnO films as a function of reactant vapor pressure.

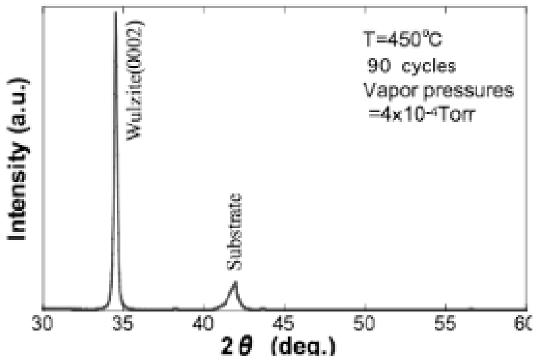

Fig. 4 XRD spectrum of ZnO film.

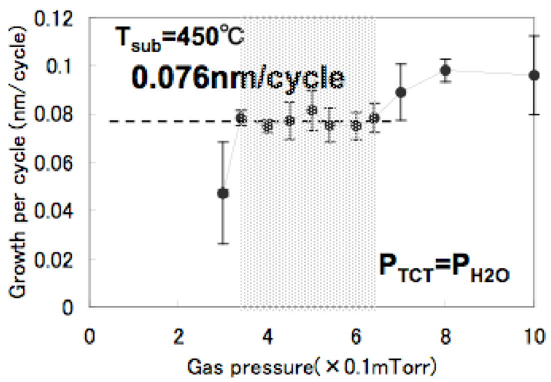

Fig. 5 Growth rate of TiO_2 films as a function of reactant vapor pressure.

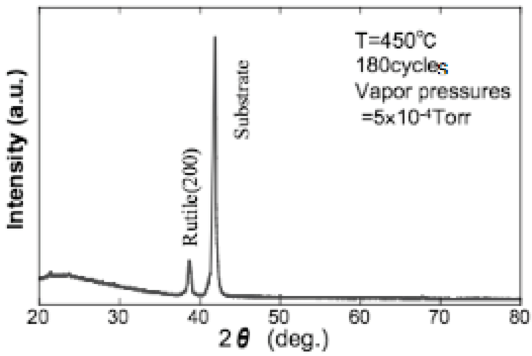

Fig. 6. XRD spectrum of TiO_2 film.

4. FABRICATION OF 10-BILAYER TiO_2/ZnO MULTILAYER

We prepared a 10-bilayer TiO_2/ZnO multilayer at a substrate temperature of 450 °C. This multilayer consists of 10 pairs of 30 cycles TiO_2 layer and 20 cycles ZnO layer, so target layer-pair thickness is 7.48 nm (30 cycles x 0.076 nm/cycle for TiO_2 + 20 cycles x 0.26 nm/cycle for ZnO).

Figure 7 shows the result of low-angle XRD measurement of this multilayer. The thickness of layer-pair can be determined from low-angle XRD measurement using the Bragg relationship ($n\lambda=2d\sin\theta$), where n is the diffraction order, λ is the wavelength, d is the thickness of layer-pair, θ is peak position of the Bragg reflection. The first Bragg peak is observed at a grazing angle of 2θ =0.606°, which corresponds to the layer-pair thickness of 14.58 nm. The reason why the measured layer-pair thickness is larger than that of calculated is not understood, but the growth rate may depend on the surface [10]. Figure 8 shows the result of measured reflectivity of this fabricated multilayer. The peak reflectivity is 9.6% at the wavelength of around 2.73 nm and a grazing angle of 2θ =9.5°. The reason why the peak reflectivity is observed at the wavelength of around 2.73 nm is because this multilayer mirror uses anomalous dispersion around Ti absorption edge (2.73 nm).

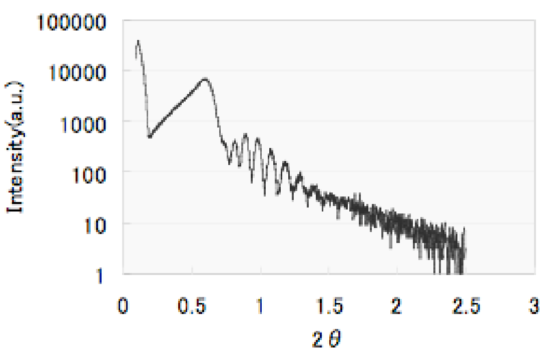

Fig. 7. Low-angle XRD spectrum of fabricated 10-bilayer TiO_2/ZnO multilayer.

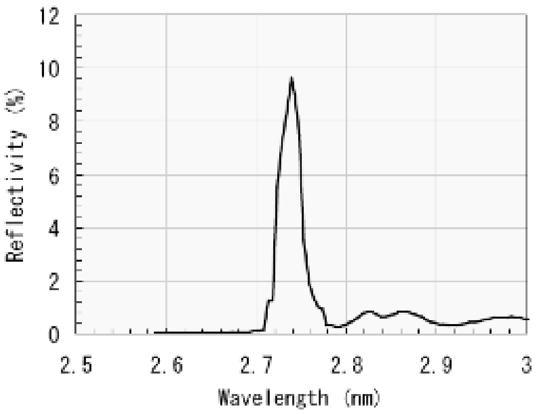

Fig. 8 Experimental reflectivity of fabricated 10-bilayer TiO_2/ZnO multilayer.

5. CONCLUSION

ZnO and TiO_2 films were grown on sapphire (0001) substrate using ALE technique at a substrate temperature of 450°C. These films were observed self-limiting growth. The ZnO films were deposited using DEZ and H_2O and it displayed a growth rate of nearly 0.26 nm/cycle. The TiO_2 films were deposited using TCT and H_2O and it displayed a growth rate of nearly 0.076 nm/cycle.

We proposed and then fabricated 10-bilayer TiO_2/ZnO multilayer mirror using ALE technique at a substrate temperature of 450°C. This multilayer achieved reflectivity of 9.6% at the wavelength of around 2.73 nm and a grazing angle of 2θ =9.5°. The growth rates of ZnO and TiO_2 in the multilayer were different from those in single layer films because the growth rate depends on used substrate. The TiO_2/ZnO multilayer will be useful for soft X-ray mirror if further studies are conducted in terms of growth rate, interface, surface roughness, and reactant vapors.

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