TiO$_2$/sapphire Beam Splitter for High-order Harmonics

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TiO$_2$/sapphire beam splitter (BS) for high-order harmonics was studied and fabricated through taking advantage of the self-limiting nature of atomic layer epitaxy (ALE). Theoretical calculation indicated that the highest reflectivity of the TiO$_2$/sapphire BS was 44.8 % at 21.24 nm, which corresponds to the 37th-order harmonics of the 800-nm pump pulse and then the optimal thickness of the TiO$_2$ layer was 67.4 nm. Incident angle was set at 70.5° for TiO$_2$, which corresponds to the Brewster's angle of the 800-nm pump pulse. Moreover, experimental results indicated that refractive indices (λ = 632.8nm) of the TiO$_2$ films were almost constant at a value of 2.59 and growth rate of TiO$_2$ films was 0.077nm/cycle, which corresponds to 885 cycles in order to deposit the TiO$_2$ layer with the optimal film thickness as an anti-reflection layer.

Keywords: titanium oxide, sapphire, beam splitter, high-order harmonics, atomic layer deposition, atomic layer epitaxy

1. Introduction

High-intensity high-order harmonic generation has been investigated intensively in recent years because of application to nonlinear optics with magnificent spatial coherence and with an ultrashort pulse duration for high peak power. In the development of beam line for high-intensity high-order harmonics, however, utilizing a conventional beam splitter (BS) (Si or SiC) that absorbs fundamental waves causes serious problems such as its thermal distortion [1]. To solve these problems, we proposed and investigated novel BS with transparent materials that transmitted the fundamental waves and then reflected the high-order harmonics. In BS for the high-order harmonics, reflection of the fundamental waves should be prevented by entering the p-polarized fundamental waves at the Brewster's angle θ_B, which could improve separation between the fundamental waves and the high-order harmonics.

Atomic layer deposition (ALD) and atomic layer epitaxy (ALE) are gas phase deposition methods that are based on sequential surface chemical reaction where the growth rate is dependent solely on the number of growth cycles. These deposition methods have emerged as the excellent techniques to fabricate a wide variety of thin films [2-6]. The main difference between ALE and chemical vapor deposition (CVD) is the way to introduce precursor into the reaction chamber. Unlike CVD, each precursor is alternately pulsed to the chamber in ALE process. ALE has self-limiting nature of the surface saturation, allowing the formation of a full or a submonolayer of atoms because adsorption of precursor gases stops due to covered surface reactive sites or steric hindrances of ligands of adsorbed

molecules. It can coat complex shapes with excellent uniformity and control thickness with precision over large areas.

We have already studied and fabricated TiO_2 thin films on sapphire (0001) substrates by controlled growth with ALD or ALE. One of authors has already demonstrated that rutile TiO_2 (200) thin films were grown epitaxially on sapphire (0001) substrates by ALE using sequentially fast pressurized titanium tetrachloride ($TiCl_4$) and water (H_2O) vapor pulses [7].

In order to achieve higher reflectivity of the high-order harmonics with BS, incident angle θ_B is required to be an approximately normal incident angle. Thus, it is desirable for transparent material to the visible light, which has large refractive index for the 800-nm pump pulse. Then, we chose and investigated rutile TiO_2 which had a large refractive index of approximately 2.8 for the 800-nm pump pulse as a novel BS with transparency materials in this study. Fig. 1 shows the structure of rutile TiO_2.
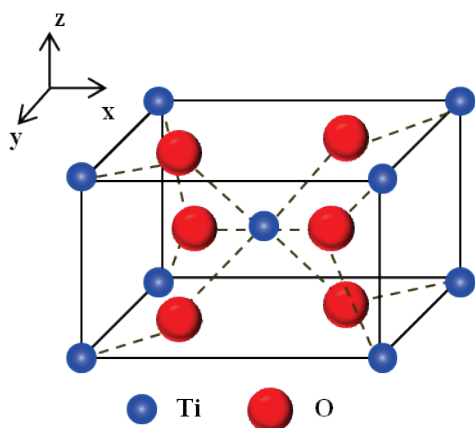

Fig. 1　Crystalline structure of rutile TiO_2

2.　Design of TiO_2/sapphire BS

The followings are two setups required in order to design TiO_2/sapphire BS for high-order harmonics.

2.1　Setup of incident angle θ_B

First of all, incident angle θ_B was set up in order to achieve high reflectivity at extreme-ultraviolet (XUV) wavelengths. Figure 2 shows theoretical reflectivity (p polarization) of TiO_2/sapphire BS [8]. Incident angle θ_B was set at 70.5° for TiO_2 and at 65.56° for sapphire, which corresponded to the Brewster angles θ_B of the 800-nm pump pulse. As shown in Fig. 2, theoretical calculation indicated that the peak reflectivities of TiO_2/sapphire BS were 44.8% (incident angle θ_B =70.5° for TiO_2) and 31.9% (incident angle θ_B =65.56° for sapphire) at 21.24 nm, which corresponded to the 37th-order harmonics of the 800-nm pump pulse, respectively. Thus, the incident angle θ_B was set at 70.5° for TiO_2, which corresponded to the Brewster angle θ_B of the 800-nm pump pulse.
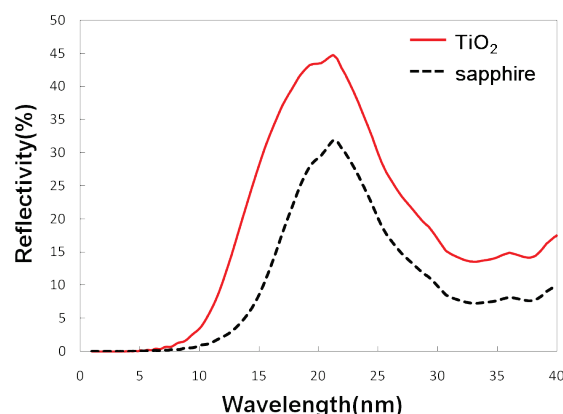

Fig. 2　Theoretical reflectivities of TiO_2/sapphire BS at the Brewster angles for TiO_2 (solid line) and sapphire (dashed line) at the pump pulse.

2.2　Setup of optimal film thickness of TiO_2 layer

As described in the previous section, the incident angle θ_B was set up in order to achieve the high reflectivity at XUV wavelengths. However, the setup to prevent reflection of the fundamental waves was not considered. Thus, we proposed that reflection of the fundamental waves was prevented by utilizing characteristic of "anti-reflection" (AR) layer controlling the film thickness of deposited TiO_2 layer. Figure 3 shows the principle of AR film. By making optical path difference between beam reflected on film surface and on the surface $\lambda/2$, phase of beam reflected on

the surface is out of phase with that of beam reflected on film surface by $\lambda/2$. As a result, reduction of reflection coefficient causes anti-reflection effect. Optimal film thickness of TiO_2 layer d_{AR} is given by $d_{AR}=\lambda\cos\theta/4n_{AR}$ (Eq.1), here d_{AR} is optimal film thickness of TiO_2 layer (AR layer), λ is wavelength of the 800 nm pump pulse, and n_{AR} is refractive index of material deposited as AR layer. Refraction angle θ is given by $\theta=\sin^{-1}(\sin\theta_B/n_{AR})$ (Eq. 2), which is known as Snell's law. Substituting the value of Brewster's angle θ_B for TiO_2 (θ_B=70.5°) and refractive index n_{AR} (n_{AR}=2.8) in Eq. 2 obtained refraction angle θ = 19.7°. Thus, optimal thickness d_{AR}=67.4 nm is obtained from Eq. 2. This value of optimal thickness d_{AR} indicated that depositing AR layer is required to control film thickness in nanometers. For practical use of BS for the high-order harmonics, we must fabricate extremely flat materials with low surface roughness on substrate. Thus, we proposed and fabricated TiO_2/sapphire BS for the high-order harmonics utilizing ALD or ALE technique in this study.
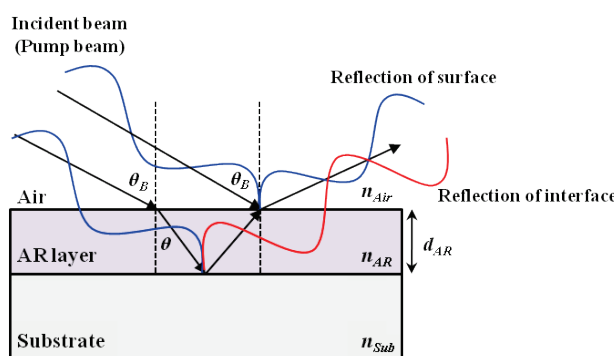
3. Experimental

The schematic diagram of the experimental apparatus is presented in Fig.4. It consists of three computer–controlled leak valves, a stainless-steel vacuum chamber, a turbo molecular pump (TMP), a capacitor manometer, an infrared-ray heater and a cold cathode gauge. The vacuum chamber was evacuated by a turbo molecular pump (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.

As a substrate, sapphire (0001) was used. To obtain clean surface, the substrate was ultrasonically cleaned in acetone. 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 TCT, 2 s evacuation, 1 s dosing of H_2O, and 2 s evacuation. One growth cycle takes 6 s. Fig. 5 shows the precursor, TCT 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 of the single layer films deposited by ALE was measured by a variable angle spectroscopic ellipsometer.
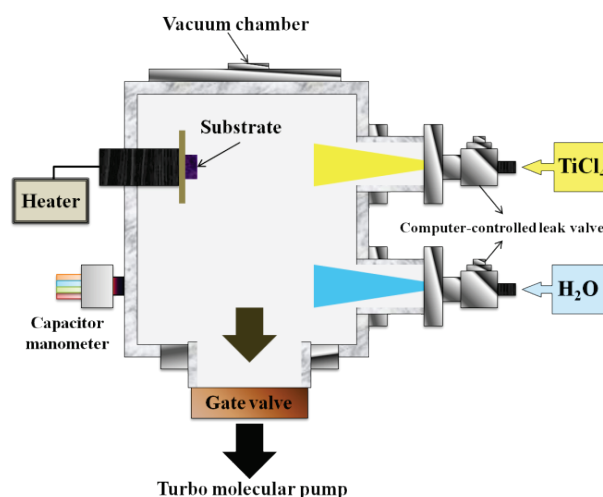

Fig. 3 Principle of AR film

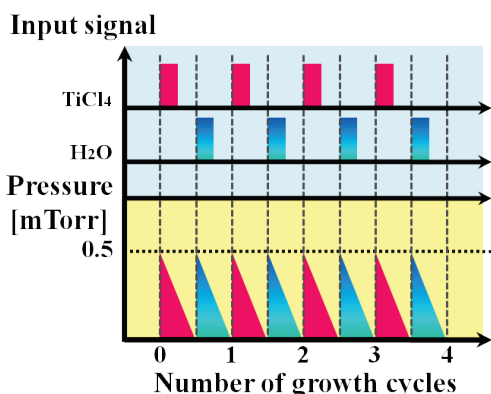**Fig. 4** Schematic diagram of the experimental apparatus for ALE.

Fig. 5 Schematic diagram of input signals applied on the computer controlled leak valves.

4. Results and discussion

Fig. 6 shows the film thickness of TiO_2 film as a function of number of growth cycles. As shown in Fig. 6, the thickness of the TiO_2 film on sapphire (0001) increased with increase in number of growth cycles when the substrate temperature was 450℃ and vapor pressure of $TiCl_4$ and H_2O was 5×10^{-4} Torr. The growth rate was constant at 0.077nm/cycle. This result indicated that growth rate of TiO_2 film can be controlled by the number of cycles with the accuracy of one-third the length of the rutile (200) monolayer. Refractive indices ($\lambda = 632.8nm$) of TiO_2 films as a function of number of growth cycles are also shown in Fig. 6. The experimental conditions were the same as those in the case of the film thickness. The refractive indices were almost constant at a value of 2.59, which nearly corresponds to the refractive index ($\lambda = 632.8nm$) of rutile TiO_2.

Fig. 7 shows that plots of growth rate and refractive indices ($\lambda = 632.8nm$) of TiO_2 films on sapphire (0001) as a function of vapor pressures of $TiCl_4$ and H_2O. The number of growth cycles was 180, and the substrate temperature was 450℃. As shown in Fig.7, the growth rate of TiO_2 was found to be approximately 0.077nm/cycle when the vapor pressures of $TiCl_4$ and H_2O are between 3.4×10^{-4}Torr and 6.4×10^{-4}Torr. Then, the growth rate was

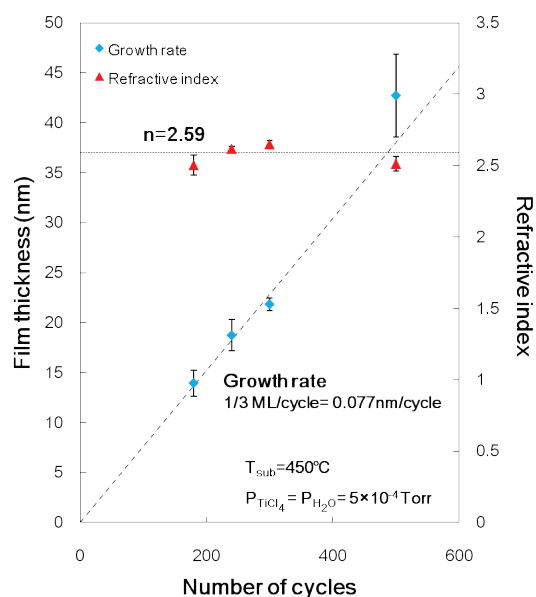considerably enhanced by increasing vapor pressure from 7×10^{-4} Torr to 15×10^{-4} Torr.

Fig. 6 Plots of thickness of TiO_2 films and refractive index as a function of number of cycles. The vapor pressure of $TiCl_4$ and H_2O was 5×10^{-4} Torr. The substrate temperature was constant at 450℃.

Constant growth rate of 0.077nm/cycle and refractive indices ($\lambda = 632.8nm$) of 2.59 was obtained in the vapor pressure range from 3.4×10^{-4}Torr to 6.4×10^{-4}Torr. The values of this growth rate and refractive indices almost correspond to one-third the length of TiO_2 (100) monolayer and the refractive index of a TiO_2 bulk crystal respectively [9]. The growth rate that was smaller than a monolayer might be due to steric exclusion of Cl ligands [10]. These results indicated that self-limiting nature seems to be involved in vapor pressure range from 3.4×10^{-4}Torr to 6.4×10^{-4}Torr because of saturated surface reactions. These experimental results indicated that taking advantage of self-limiting nature of ALE, TiO_2/sapphire thin films which have high reflectivity can be fabricated as BS for high-order harmonics.

Moreover, the value of growth rate 0.077nm/cycle derived that of 885 cycles, that is total number of growth
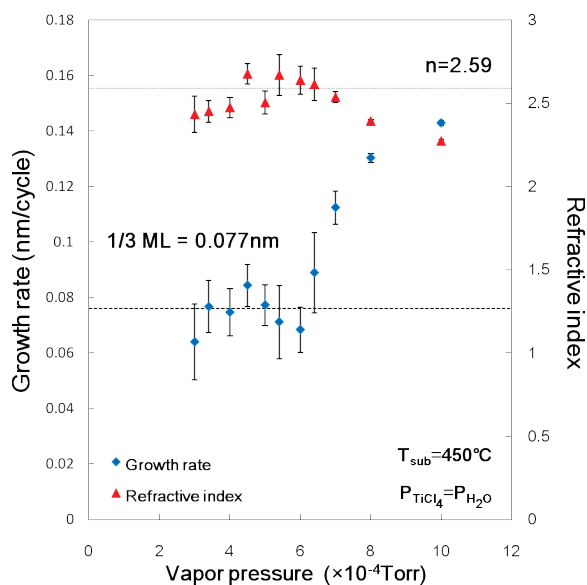
Fig. 7 Plots of growth rate and refractive index of TiO_2 films as a function of reactant vapor pressure. The vapor pressures of $TiCl_4$ and H_2O were the same. The substrate temperature was constant at 450℃.

cycles required to deposit TiO_2 layer (AR layer) of optimal thickness d_{AR}=67.4 nm which was obtained from Eq. 2.

5. Conclusion

TiO_2/sapphire beam splitter for high-order harmonics was studied and fabricated taking advantage of self-limiting nature of atomic layer epitaxy (ALE). For the self-limiting region, growth rate was almost constant at a value of 0.077nm/cycle, and refractive indices (λ = 632.8nm) were also constant at 2.59 at a substrate temperature of 450 ℃. Theoretical calculation indicated that peak reflectivity of TiO_2/sapphire BS was high reflectivity of 44.8 % at 21.24 nm, which corresponds 37th order harmonics of the 800 nm pump pulse and optimal thickness of TiO_2 layer was 67.4 nm. Incident angle was set at 70.5° for TiO_2, which corresponds to the Brewster's angle of the 800 nm pump pulse. Moreover, experimental results indicated that refractive indices (λ = 632.8nm) of TiO_2 films were almost constant at a value of 2.59 and growth rate of TiO_2 films was 0.077nm/cycle, which corresponds to 885 cycles in

order to deposit TiO_2 layer as anti-reflection layer of optimal film thickness.

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