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Growth of oriented LaF_3 thin films on Si (100) substrates by the pulsed laser deposition method

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Abstract LaF_3 thin films have been fabricated on Si (100) substrates under the highest possible vacuum condition by pulsed laser deposition (PLD) method. The temperature of the sbustrate varied from 20°C to 800°C. The films deposited at the higher temperature indicated the sharper peaks in the X-ray diffraction measurement. A highly oriented film was successfully obtained at a substrate temperature of 800°C. The surface observation by the AFM revealed that the many hexagonal structures constructed the film. The XPS analysis revealed that the lacking of F in the film deposited at 600°C were much more than that in film at 20°C. Adding the adequate amount of CF_4 gas in the growth chamber can compensate this lacking of F.

Key words Thin film, Lanthanum trifluoride (LaF_3), Pulsed laser deposition (PLD) method, KrF excimer laser, Orientated film

1. Introduction

Fluoride films on semiconductors are attracting interest for applications such as dielectrics in field-effect transitions, insulators in three-dimensional integrated circuits and waveguides. Expecially, fluorides of trivalent metals are water insoluble, and physical durability is better than those of divalent metals. So they are considered to be candidates for the practical applications.

Generally, in the film growth process of fluorides, since the contamination of oxygen and carbon often become a problem, the molecular beam epitaxy (MBE) under the ultra-high vacuum condition have been tried to fabricate the fluoride films [1-9]. However, the relatively large scale and complicated equipments are necessary for the MBE growth. In this paper, we report the film growth of LaF_3 on Si (100) substrate by the pulsed laser deposition (PLD) method, which needs very simple equipment compared to the MBE method. As a result, highly oriented films were obtained by setting the substrate temperature up to 800°C in the vacuum condition of 10^{-9} Torr.

2. Experimental Equipment and Procedure

Equipment used in the present experiments is schematically shown in Fig. 1. The size of the chamber was 320 mm in diameter and 150 mm in hight. In order to achieve the impurity content of the atmosphere in the chamber as low as possible, we evacuated the chamber using a combination of a rotary pump (pumping speed: 120 l/min) and two turbo molecular pumps (pumping speed: 50 l/sec and 300 l/sec, respectively) connected in tandem. The baking for 12 hours allowed of performing the film fabrication experiments under the pressure of approximately 10^{-9} Torr.

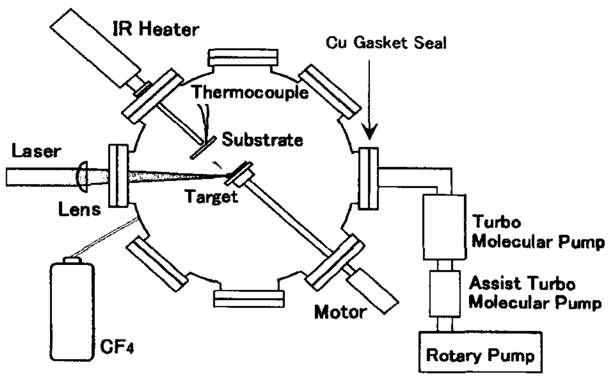

Fig. 1. A schametic drawing of experimental setup.

A KrF excimer laser (wavelength: $\lambda = 248$ nm) was used as a driving light source for the PLD method. The laser was focused on the target surface by a plano-convex lens made of synthetic silica with a focal length of 400 mm. The laser was irradiated at 45° from the target normal.

A single crystalline LaF_3 was used as a target. Si (100)

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Table 1
The experimental conditions

Laser	KrF excimer laser	
Fluence	5.0 J/cm^2	
Number of shots	50,000 Shots	
Target	Single crystalline LaF_3	
Substrate	Si (100)	
Target-substrate distance	30 min	
	The pressure	The temperature of substrate
The influence of the cleanliness in chamber	10^{-3} Torr 10^{-5} Torr 10^{-9} Torr	R.T
The influence of the temperature of substarate	10^{-9} Torr	R.T 400°C 500°C 600°C 800°C
The influence of the addition of CF_4 Gas	10^{-8} Torr	600°C 800°C

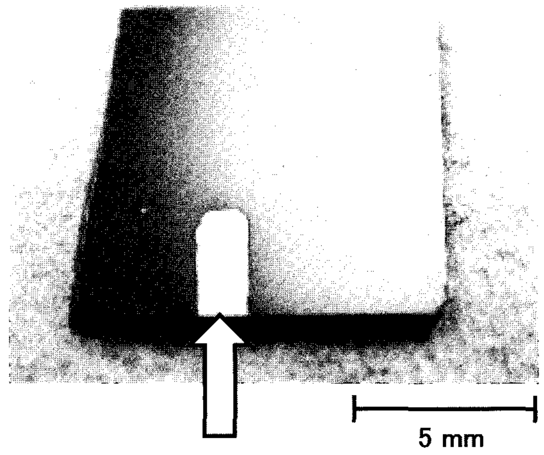

Fig. 2. A photograph of typical LaF_3 film deposited by this work.

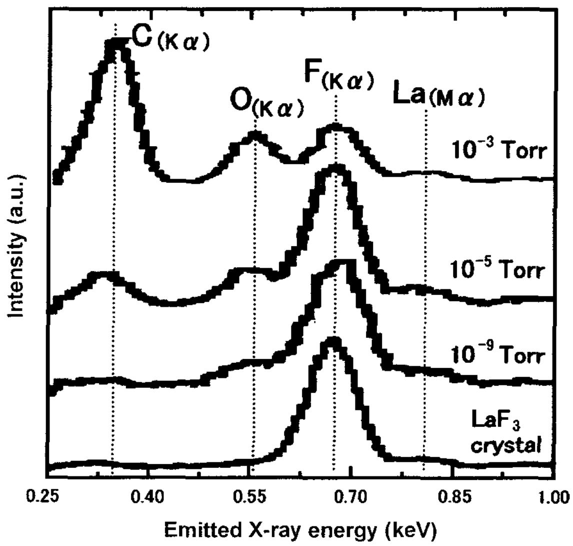

Fig. 3. The result of the EPMA measurement for the films deposited under the different base pressures.

plates were used as substrates. The temperature of the substrate was raised and controlled by a combination of an infrared heating system and a temperature comptroller with the Pt-PtRh thermocouple. The substrate was located parallel to the target surface. The distance between the target and the substrate was 30 mm. The experimental conditions for the film fabrication are summarized in Table 1.

The fabricated film was characterized with an electron-photoemission micro analyzer (EPMA), an X-ray diffractometer (XRD), an atomic force microscope (AFM), and an X-ray photoelectron spectrometer (XPS).

3. Results and Discussions

3.1. The effect of the base pressure

A photograph of a typical film fabricated by the present experiment is shown in Fig. 2. Glossy films with thickness of 100~200 nm were obtained by 50,000 shots of the laser irradiation. The EPMA and XRD spectra for the films which fabricated by changing the base pressure in the range indicated in Table 1 was shown in Fig. 3 and Fig. 4, respectively. Proceeding to the EPMA measurement, the films were coated with gold of 10 nm thick in order to prevent the charging up. The acceleration voltage of 20 kV was adopted. Considerable amount of C and O were detected for the film fabricated at a base pressure of 10^{-3} Torr, which is achieved by using only the rotary pump. As decreasing the pressure, the amount of C and O rapidly decreased. When the pressure is 10^{-9} Torr, only traceable amount of C and O were detected. Decreasing the pressure, the XRD spectra had a tendency to become sharper as shown in Fig. 4. From these results, it can be said that the smaller the impurity, the higher the crystallinity can be achieved, because the bonding to construct LaF_3 structure may not be disturbed by the impurities. In the case of 10^{-9} Torr, the largest peak seemed to be from (111) face, which is corresponding to the largest peak in the diffraction pattern in LaF_3 powder. Beside this, the peaks corresponded to (002), (110) have also been observed. This fact may suggest that the almost randomly oriented

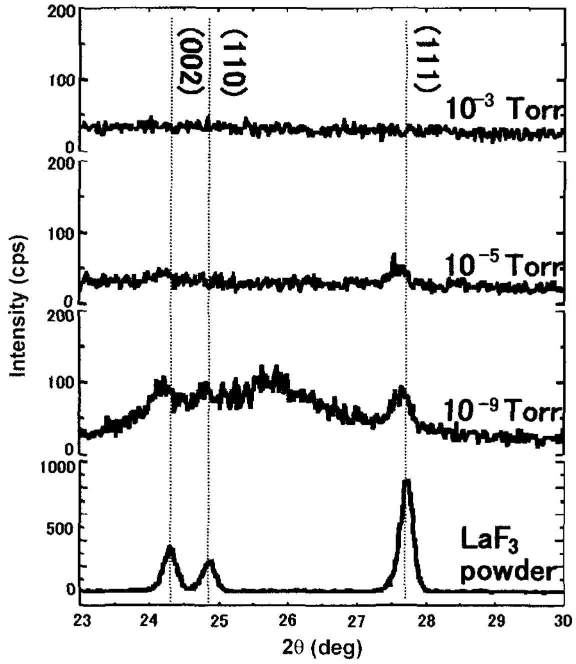

Fig. 4. The result of the XRD analysis for the films deposited under the different base pressure at room temperature.

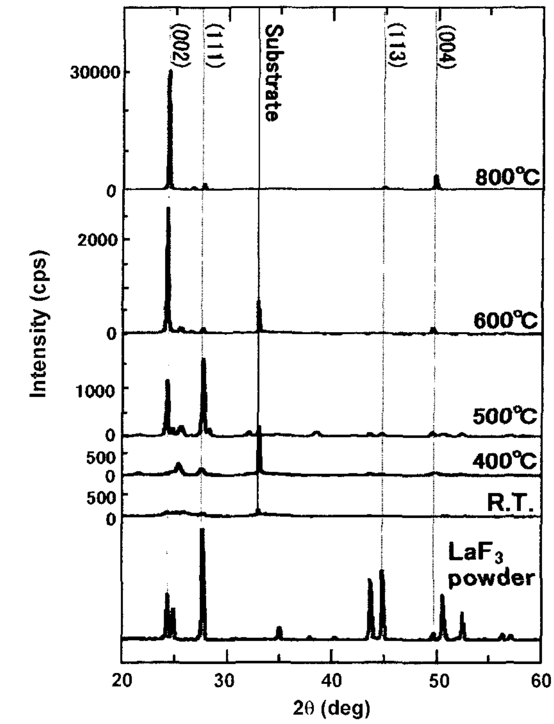

Fig. 5. The result of the XRD analysis for the films deposited at different temperature under a pressure of 10^{-9} Torr.

polycrystalline films have been fabricated at R.T.

3.2. *Influence of the substrate temperature*

Since the reducing of impurities in the films has been successfully achieved by reducing the pressure in the chamber, next, we concentrated to treat the crystallinity of the film. We performed the experiments by changing the temperature of the substrates in the range indicated in Table 2. All these experiments were carried out at a pressure of 10^{-9} Torr. Figure 5 shows the θ-2θ scanning results consistent with the results shown in Fig. 4. The voltage and the tube current were 40 kV and 100 mA, respectively. The higher the temperature, the higher the crystallinity has been obtained. Below 500°C, the intensity from (111) plane was the largest. This means a strong orientation does not occur at this temperature range. In contrast, above 600°C, the peak from (002) plane become very strong and (111) peak was almost disappeared. This fact indicates a strong orientation of film in (001) direction. Of course these results do not simply mean the presence of single crystalline films or perfect epitaxial growth, however, it is remarkable that the (001) face of LaF_3 which has a hexagonal structure has been connected compatibly with the (100) face of Si which has a tetragonal structure at the substrate temperature of 800°C.

Table 2
Ratio of La and F in the fabricated films measured by the XPS

	R.T	600°C	800°C
10^{-9} Torr	1:1.53	1:0.82	1:1.40
Added CF_4 of 10^{-8} Torr		1:1.60	1:1.44

AFM images of the film fabricated at 500°C~800°C were indicated in Fig. 6. In Fig. 6(a), several roundish hillocks with a diameter of a few micrometers were observed. At 600°C, a number of small roundish hillocks with diameter of 0.05~0.3 μm were formed, and top of the relatively larger hillocks were flattened as shown in Fig. 6(b). Furthermore, this tendency became stronger at 800°C, and resulted in forming the flat hexagonal layers as shown in Fig. 6(c). Since the (001) face of LaF_3 has a 6-fold axis, these observations quite correspond with the results in Fig. 5.

Next, we will discuss about the reason that the hexagonal (001) LaF_3 film has become oriented on the cubic Si (100) surface. Figure 7 shows schematic structure of Si (100) and LaF_3 (001) faces drawn in the same scale. The detailed structure of LaF_3 is still having an ambiguity. There have been many papers which the different stucture, e.g. $P6_3/mcm$ [10], $P3c1$ [11-12], $P6_3cm$ [13], $P6_3/mmc$ [14], and so on. However, all reported structures are hexagonal or the similar structure. Hence, in Fig. 7, right hexagonal with a side 7.19 Å long that is

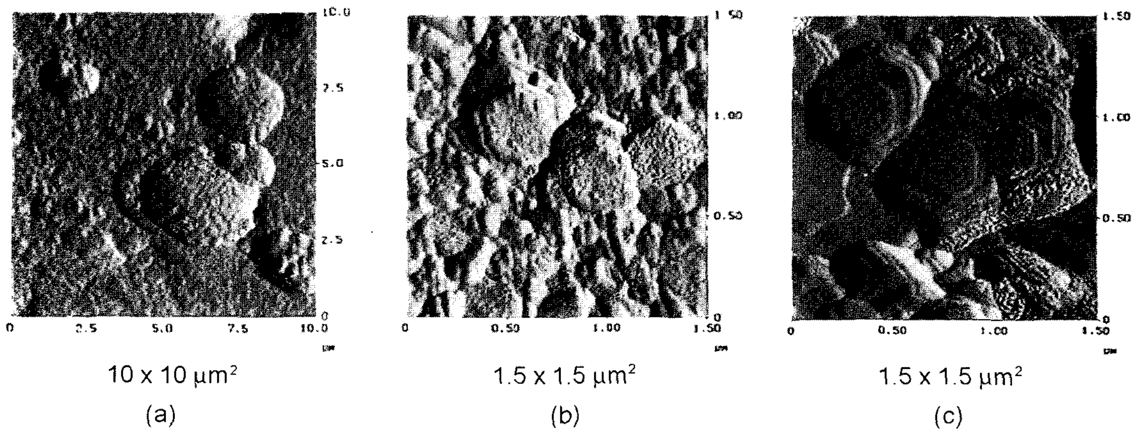

Fig. 6. The images of the film surface obsered by AFM (differenteal image).

listed in the JCPDS card have been illustrated. In the horizontal direction in Fig. 7, three times the length of the *a*-axis of a LaF_3 unit cell almost matches four times that of a Si unit cell (The mismatch is 0.7%). In the vertical direction in Fig. 7, the seven times the interplanar spacing of Si (020) almost matches the three times that of LaF_3 (010) (The mismatch is 1.7%). We consider that this periodical agreement should be a reason why the strong oriented LaF_3 films have been formed on the Si (100) substrates.

3.3. *The effect of the additive gas*

The results of composition analysis by the XPS for the films that had been fabricated in 10^{-9} Torr with the elevated temperatures were shown in Table 2. Proceeding to the XPS measurement the surface of the samples was etched by Ar beam in the XPS chamber. The absolute values in Table 2 cannot be trusted because the correction for the absolute value is very difficult in our XPS equipment at the present moment. However, we caught a qualitative tendency that the lack of F is increasing when the film is deposited at the elevated temperature. This tendency was the biggest when the temperature was 600°C in which the crystal perfection and the XRD peak intensity of (002) plane is relatively low. To compensate the lacking of F, we tried to add the CF_4 gas of 10^{-8} Torr in the chamber during the film deposition. The results are also shown in Table 2. The ratio of La to F was successfully improved for both films deposited at 600°C and 800°C. Especially in the case of 600°C, the effect of additive gas seemed to be more effective compared to the case of 800°C in which the very sharp XRD peak had already been obtained even if

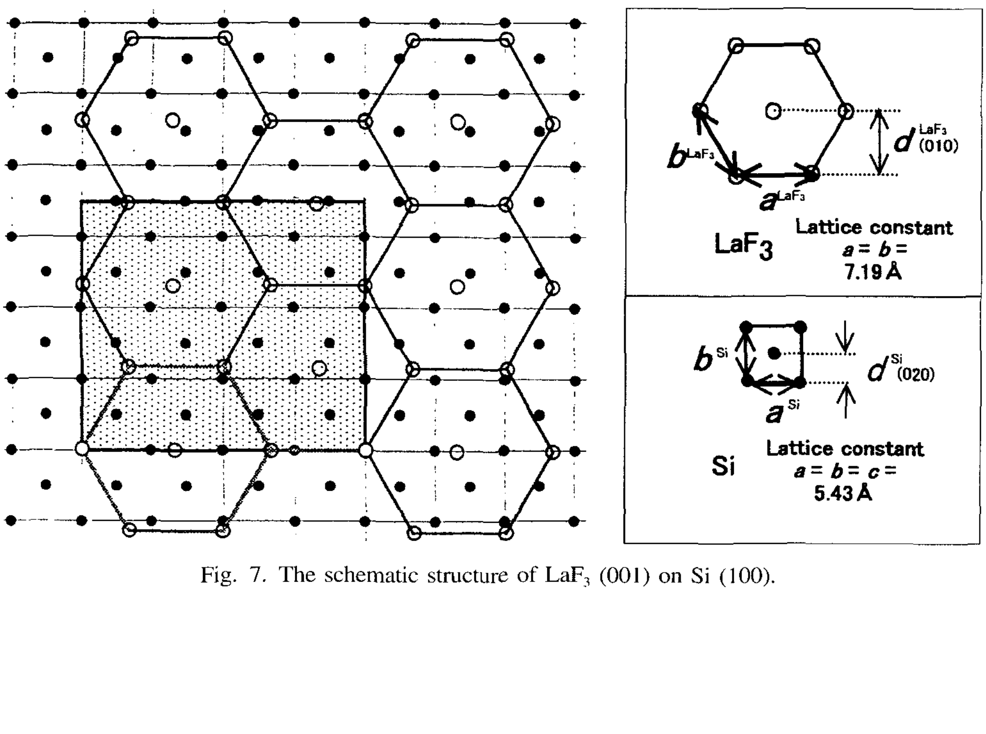

Fig. 7. The schematic structure of LaF_3 (001) on Si (100).

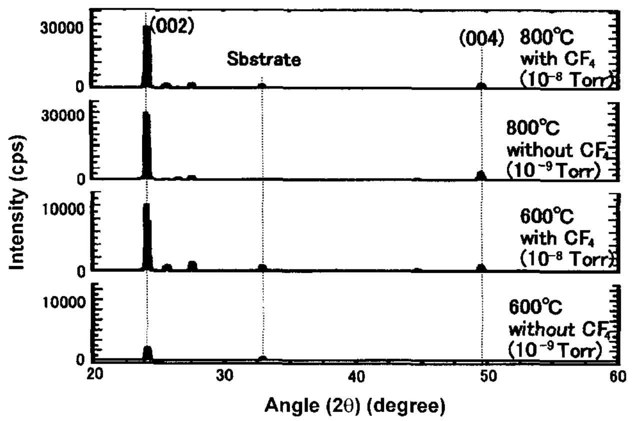

Fig. 8. The influence of addition of CF_4 gas during deposition.

no additive gas was introduced. The XRD spectra of the films with and without the additive gas were shown in Fig. 8. However only the small changes were observed at 800°C, the peak intensity of (002) face of the added film became almost five times larger than the unadded film in the case of at 600°C.

We considered that the F atoms from CF_4 compensated the F vacancies which exists a lot in the unadded film deposited at 600°C and then improved the crystallinity of the film. Optimizing the concentration of CF_4 gas, we consider that a highly oriented film can be obtained at the temperature lower than 800°C.

4. Conclusion

We have tried to fabricate LaF_3 thin films on the Si (100) substrate by the PLD method under the highest possible vacuum condition. As a result highly (001) oriented LaF_3 film could be grown at a substrate temperature of 800°C under the pressure of 10^{-9} Torr. The XPS analysis revealed the lack of F in the films deposited at the elevated temperature. This lacking was found to be compensated by adding the adequate amount of CF_4 gas. These results are very promising to simplify the process of semiconductor devices utilizing the fluorides for next generation.

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