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Preparation of $PbTiO_3$ thin films by plasma- and photo-assisted CVD

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$PbTiO_3$ thin film was prepared by plasma- and photo-assisted CVD. Pb/(Pb+Ti) in the film increased by the irradiation of the Xe-Hg lamp (200W). The films with Pb/(Pb+Ti) of 0.5 was obtained even at 380 ℃, but the constituent phase of this film was mainly PbO together with the minor $PbTiO_3$.
On the other hand, when the plasma was irradiated into the source gas just before the substrate, Pb/(Pb+Ti) increased with the increase of the plasma power up to 80W at 380 ℃. When plasma was irradiated together with the laser, (100) oriented $PbTiO_3$ film was deposited, while polycrystalline $PbTiO_3$ phase was deposited when only laser was irradiated.

1.Introduction

$Pb(Zr,Ti)O_3$ films have been widely studied for a variety of electrical and optical applications because of its excellent dielectric and piezoelectric properties. The film with good electrical properties was reported to be deposited between 550° and 700 ℃ by CVD. However, the deposition below 550 ℃ has been hardly reported. This is mainly owing to the decrease of the crystallinity of the film with decreasing deposition temperature and the codeposition of other phase . The introduction of the excitation process to the conventional deposition process is considered to be effective to get the film with high crystallinity at lower temperature. In the previous study, KrF excimer laser was irradiated perpendicular to the surface of the substrate under the conventional thermal CVD process and the crystalline $PbTiO_3$ film was deposited at 380 ℃[1].

In the present study, we tried to prepared $PbTiO_3$ films by plasma-assisted CVD and Xe-Hg lamp-assisted CVD together with laser-assisted CVD and observed the improvement of the crystallinity, composition and the microstructure of the films of these irradiations.

2.Experimental Procedure

Fig.1 shows the schematic diagram of the reaction chamber for the plasma-assisted, Xe-Hg lamp-assisted and laser-assisted CVD. Source materials for the deposition were $Pb(C_{11}H_{19}O_2)_2$, Ti(O-i-C_3H_7)4 and O_2, and the substrate was (111) $Pt/SiO_2/Si$. As shown Fig.1, RF plasma was irradiated into the source gas just before the substrate. The irradiation of RF plasma at this position is expected to accelerate the decomposition of source gases but not to diminish a damage of the surface of the substrate. Xe-Hg lamp (Hamamatsu photonics, co.ltd, C-2423,

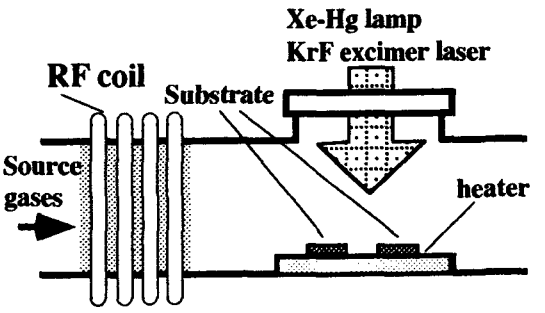

Fig. 1 Schematic diagram of RF plasma-assisted, Xe-Hg lamp-assisted and laser assisted CVD apparatus.

200W) and KrF eximer laser were irradiated perpendicular to the surface of the substrate through a fused silica window. Deposition and irradiation conditions are summarized in Table 1.

The constituent phase, crystallinity and the orientation of the film was observed by XRD. The microstructure and the composition were observed by SEM and EDS attached to SEM, respectively. We have already ascertained by using the standard sample that the peak intensities were proportional to the deposition amount.

3. Results and Discussion

3.1. Irradiation of Xe-Hg lamp

Fig.2 shows the XRD patterns of the films deposited (a)with (Lamp on) and (b) without (Lamp off) Xe-Hg lamp irradiation at 380 ℃. Fig.2 also shows that of the film deposited with (c)KrF laser irradiation(Laser on). Pb/(Pb+Ti) of (a) and (c) were almost 0.5. On the other hand, Pb/(Pb+Ti) of (c) was almost constant to be 0.4 up to 0.95 of the carrier gas flow rate fraction, $[Pb(C_{11}H_{19}O_2)_2]/[(Pb(C_{11}H_{19}O_2)$

Table 1 Deposition condieions

Source materials, vaporizer temperature and carrier gas flow rates		
$Pb(C_{11}H_{19}O_2)_2$	141 °C	200 cm^3/min
$Ti(O\cdot i\text{-}C_3H_7)_4$	41 °C	60 cm^3/min
Deposition temperature : 380-590 °C		
Total gas pressure	: 5.0 Torr(pO_2 : 2.5 Torr)	
Deposition time	: 120 min	
UV light	Source light	: Xe-Hg lamp
	Power	: 200 W
RF plasma	Radio frequency	: 13.56 MHz
	Power	: 0-80 W
Laser	Wave length	: 248 nm(KrF)
	Puls energy	: 20 mJ/cm^2
	Repitition time	: 10 Hz

2 + $Ti(O\cdot i\text{-}C_3H_7)_4$], so that Pb/(Pb + Ti) of 0.4 is shown in Fig.2(c) . The film without Xe-Hg lamp consisted of amorphous phase as shown in Fig.2(b). On the other hand, the film deposited with Xe-Hg lamp irradiation consisted of the mixture phase of PbO and $PbTiO_3$ as shown in Fig.2(a). This is different from that of the film deposited with KrF laser irradiation, which consisted of the single phase of polycrystalline $PbTiO_3$ as shown in Fig.2(c). Therefore in the case of the film with Xe-Hg lamp

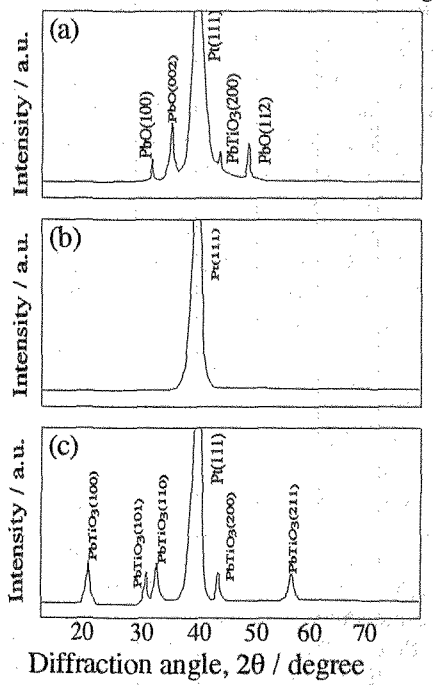

Fig.2 XRD patterns of the films prepared by (a) Xe-Hg lamp assisted-CVD and (b)thermal CVD and (c)KrF laser- assisted CVD.

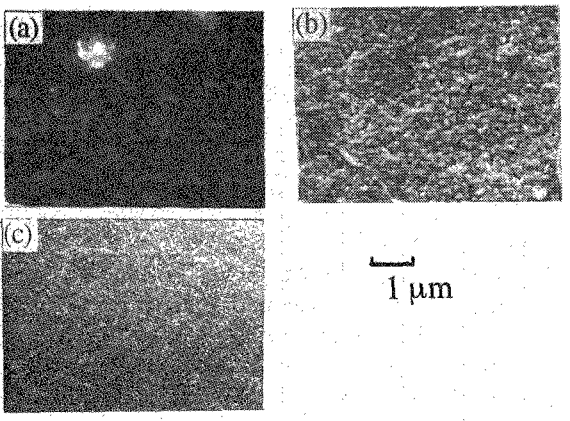

Fig.3 SEM photographs of the same films as Fig.2 prepared by (a)Xe-Hg lamp assisted-CVD and (b)thermal CVD and (c)KrF laser- assisted CVD.

irradiation, the single phase of $PbTiO_3$ was not obtained when Pb/(Pb+Ti) of the film was 0.5. Fig.3 shows the SEM photographs of the same films as Fig.2. The film with KrF laser irradiated shown in Fig.3(c) had a relatively rough surface compared with Fig.3(a) and (b). This was considered to be related to the etching by the irradiation of the high-power laser. The deposition rates of these film with Xe-Hg lamp irradiation, without irradiation and with laser irradiation were 2.8, 2.2 and 4.0 nm/min, respectively. As a result, Xe-Hg lamp irradiation increased Pb/(Pb+Ti) and the deposition rate of the film. The film with Pb/(Pb+Ti) of 0.5 and consisting of crystalline phase was obtained at 380 °C. However, it did not affect the microstructure of the film, and the constituent phase of the film with Pb/(Pb+Ti) of 0.5 was the mixture phase of PbO and $PbTiO_3$.

To make clear the effect of Xe-Hg lamp irradiation on the composition in the film, the composition of the film was father investigated as a function of the deposition temperature. Fig. 4 shows the change of Pb/(Pb + Ti) in the film as a function of deposition temperature under the carrier gas flow rate fraction of 0.80. For the film without irradiation, Pb/(Pb + Ti) increased with the deposition temperature and became constant to be 0.50 above 450 °C. In the case of the film with Xe-Hg lamp irradiation, the temperature dependency of Pb/(Pb + Ti) was almost the same as the film without the irradiation. However, Pb/(Pb + Ti) was 0.55 above 450 °C, which was higher than that without irradiation. This means that Pb/(Pb + Ti) increased with the Xe-Hg lamp irradiation and the film with 0.5 of Pb/(Pb+Ti) was obtained under the lower carrier gas flow rate fraction. It was revealed

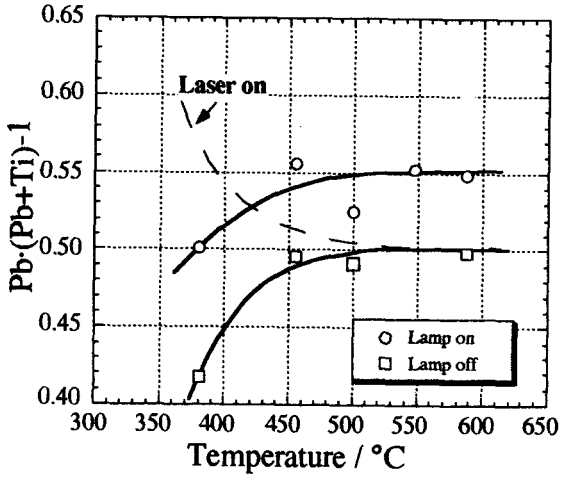

Fig.4 Change of Pb/(Pb + Ti) in the film with the deposition temperature.

from the Pb and Ti EDS peak intensities change with the deposition temperature that the increase of Pb/(Pb +Ti) by the Xe-Hg lamp irradiation was originated to both the increase of the deposition amount of Pb element and the decrease of that of Ti element. In the case of PbO and TiO_2 films from $Pb(C_{11}H_{19}O_2)_2$-O_2 and $Ti(O\text{-}i\text{-}C_3H_7)_4$, respectively, the increase of the deposition amount of Pb element by the lamp irradiation was higher than that of Ti element. This result was in good agreement with the effect by the laser irradiation.

The deposition temperature is considered to increase by the irradiation of Xe-Hg lamp irradiation. In fact, deposition temperature increase of c.a. 40 °C was observed by the irradiation of Xe-Hg lamp at room temperature. If the increase of the deposition temperature is predominate effect of the Xe-Hg lamp irradiation, the shift of Pb/(Pb+Ti) against the deposition temperature to the lower one must be observed in Fig.4. However, Pb/(Pb+Ti) of the film with laser irradiation was about 0.05 higher than that of the film without laser irradiation. Therefore, the effect of the Xe-Hg lamp irradiation is explained only by the increase of the deposition temperature.

In the case of the film with KrF laser irradiation, Pb/(Pb + Ti) decreased with the increase of the temperature up to 500 °C. This was the opposite tendency compared to the films with Xe-Hg lamp irradiation and without irradiation as shown in Fig.4. Moreover, Pb/(Pb+Ti) above 500 °C was constant to be 0.5 and was almost equal to that of the film without irradiation. This result shows that the laser irradiation effect on Pb/(Pb+Ti) was diminished above 500 °C. On the other hand, the effect of Xe-Hg lamp irradiation was still observed at this temperature

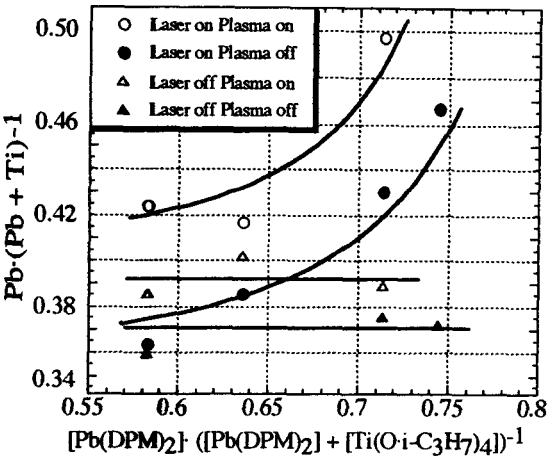

Fig. 5 The composition change of the film with the carrier gas flow rate fraction.

range. This result shows that, Xe-Hg lamp irradiation is effective compared with laser irradiation above 500 °C.

3.2 Irradiation of RF plasma and KrF laser

Fig.5 shows Pb/(Pb+Ti) in the film as a function of the carrier gas flow rate fraction under four laser and plasma irradiation conditions. Pb/(Pb+Ti) in the film increased by the plasma irradiation(80 W) regardless of the laser irradiation as shown in Fig.5. When the laser was not irradiated(Laser off), Pb/(Pb+ Ti) was almost constant with the increase of the carrier gas flow rate fraction, i.e., 0.37 for the film without the plasma irradiation(Plasma off) and 0.39 for the film with the plasma irradiation(Plasma on). When the laser was irradiated(laser on), Pb/(Pb+Ti) increased with the increase of the carrier gas flow rate fraction irrespective of the plasma irradiation. The film with Pb/(Pb+Ti) of 0.5 was obtained under the carrier gas flow rate of 0.71 and 0.75 for the film with and without plasma irradiation, respectively. This means that the film with 0.5 of Pb/(Pb+Ti) was obtained under lower carrier gas flow rate fraction by both of laser and plasma irradiation compared with the laser irradiation.

Fig.6 shows Pb/(Pb+Ti) change with the plasma power under the carrier gas flow rate fraction of 0.58. Pb/(Pb+Ti) increased with the plasma power of the plasma regardless of the laser irradiation. Moreover, Pb/(Pb+Ti) of the film with the laser irradiation was higher than that without laser irradiation. It was observed from the Pb and Ti EDS peak intensities change with plasma power that both of the deposition amounts of Pb and Ti elements increased with the increase of the plasma power.

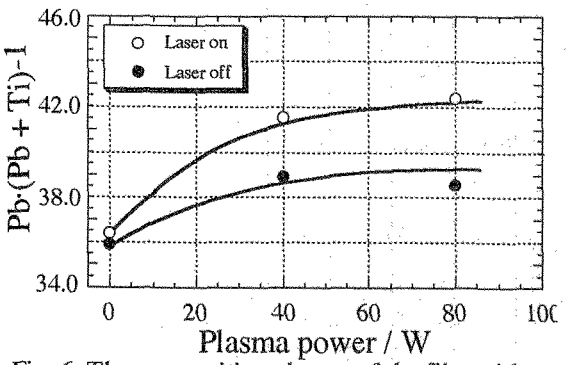

Fig. 6 The composition change of the film with the plasma power.

However, the increase of the film with laser irradiation was higher than that without laser irradiation. Moreover, that of Pb element was higher than that of Ti element. The fact that the deposition amount of Ti element increased by the plasma irradiation was different from the phenomena by the laser and Xe-Hg lamp irradiation, in which the deposition amount of Pb element increased but that of Ti element was almost constant by the irradiation.

Fig.7 shows XRD patterns of the film with (a) both of plasma and laser irradiation and (b)plasma irradiation at 380 ℃. Pb/(Pb+Ti) of (a) and (b) is 0.5 and 0.4, respectively. The film with plasma irradiation constituted of amorphous phase. This result was related to the fact that Pb/(Pb + Ti) was almost constant of about 0.4 even though the carrier gas flow rate fraction increased up to 0.71 as shown in Fig.5. On the other hand, the films with both of

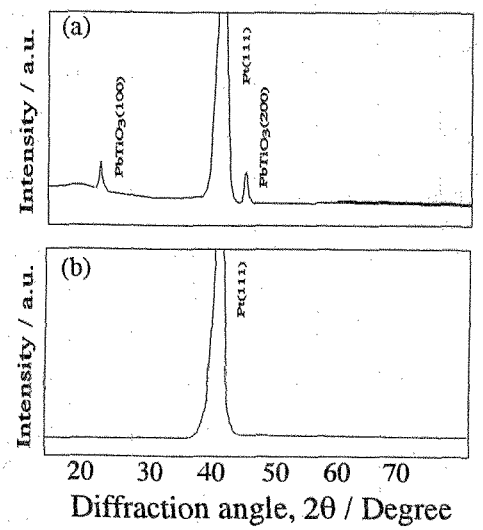

Fig.7 XRD patters of the films prepared by (a) plasma and laser-assisted CVD and (b) plasma-assisted CVD.

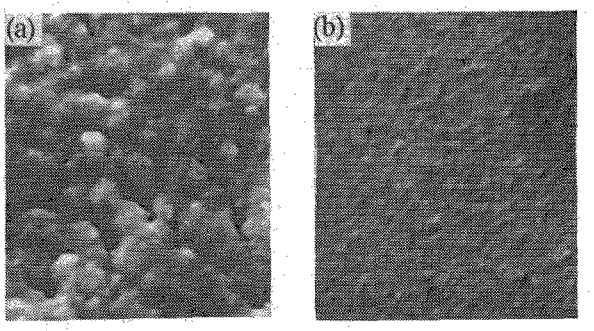

Fig.8 SEM photographs of the same films as Fig.7 prepared by (a)plasma and laser-assisted CVD and (b) plasma-assisted CVD. ⟵ 1 μm

plasma and laser irradiation and with Pb/(Pb+Ti) of 0.5 were constituted of the single phase of $PbTiO_3$ as shown in Fig.8(a). Moreover, this film oriented to (100) plane. This is different from the fact that the film with laser irradiation consisted of polycrystalline $PbTiO_3$ single phase as shown in Fig.2(c). This result shows that (100) oriented film was obtained by the plasma irradiation together with the laser irradiation.

Fig.8 shows SEM micrographs of the same films as those in Fig.7. The film with both plasma and laser irradiation made up of the large grains, about 1 μm in size. On the other hand, very smooth surface was observed for the film with plasma irradiation. This microstructure related to the fact that the constituent phase of this film was amorphous. In summary, plasma irradiation increased the deposition amount of Pb element. The film with Pb/(Pb+Ti) of 0.5 was obtained by both laser and plasma irradiation and oriented to (100) plane.

4. Conclusions

$PbTiO_3$ thin film was prepared by plasma- and photo-assisted CVD. Pb/(Pb+Ti) in the film increased by the irradiation of the Xe-Hg lamp (200W). The films with Pb/(Pb+Ti) of 0.5 was obtained even at 380 ^{OCR}, but the constituent phase of this film was mainly PbO together with the minor $PbTiO_3$. On the other hand, when the plasma was irradiated into the source gas just before the substrate, together with the laser, (100) oriented $PbTiO_3$ film was deposited, while polycrystalline $PbTiO_3$ phase was deposited when only laser was irradiated.

References

(1) Y.Yamazaki, T.Hioki, H.Funakubo, K.Shinozaki and N.Mizutani, Mater.Res.Bull., 30(9)(1995) 1081.