

## High Rate Sapphire Etching Using $\text{BCl}_3$ -Based Inductively Coupled Plasma

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Sapphire was etched in an inductively coupled plasma equipment using  $\text{BCl}_3$ -based gas combination. The etch characteristics of sapphire were investigated as functions of additive gas, inductive power, and dc bias voltage. In the case of additive gas effects, 380 nm/min of etch rate could be obtained in  $\text{BCl}_3/\text{Cl}_2$  and the anisotropic etch profile could be observed in  $\text{BCl}_3/\text{HBr}$ . From the ion saturation currents measured by Langmuir probe and optical emission intensities by OES, sapphire etch characteristics appeared to be controlled by the  $\text{BCl}$  radicals in the plasma. The effects of inductive power and dc bias voltage on the sapphire etch rate were studied in  $\text{BCl}_3/\text{HBr}/\text{Ar}$  plasmas. The results showed that the increase of inductive power and dc bias voltage increased the sapphire and photoresist etch rates almost linearly. The obtained highest sapphire etch rate in the  $\text{BCl}_3/\text{HBr}/\text{Ar}$  plasma was 550 nm/min with about 0.87 of the etch selectivity over photoresist and 75 degree of etch profile angle at 1400 Watts of inductive power and -800 Volts of dc bias voltage.

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### I. INTRODUCTION

Aluminum oxide (sapphire) is a well-known material having excellent chemical and physical stability. Therefore, it has been widely used as a hard coating material in industrial applications [1,2]. Recently, GaN-based Nitrides have become attractive materials for optoelectronic device applications such as blue light emitting diodes(LEDs) and laser diodes(LDs). Therefore, single crystal aluminum oxide (sapphire) has become more attractive materials as the substrate for GaN-based Nitrides epitaxial film growth [3-6]. But one of the problems of sapphire wafer for GaN-based optoelectronic device is the difficulty in device separation or isolation. Therefore, product yield is reduced in the final processes such as backside mechanical polishing and cutting or scribing. One of the techniques that could replace backside mechanical polishing and cutting or scribing of sapphire wafer is to use sapphire etching. To etch sapphire, several etch techniques such as ion beam etching (IBE), chemical wet etching after ion implantation, reactive ion etching, laser-assisted etching, *etc.* have been used [7-10]. In most studies of sapphire dry etching, various halogen plasmas have been used. For example, F-containing plasmas have been used. Because reaction products such as  $\text{AlF}_3$  and  $\text{Al}_x\text{O}_y\text{F}_z$  [11], *etc.* are not volatile, the reactive ion etching of  $\text{Al}_2\text{O}_3$  in F-containing plasmas

may be considered infeasible. However, the etching of  $\text{Al}_2\text{O}_3$  in F-containing plasmas has been reported to be much faster than that in Ar plasma due to high sputtering yield of  $\text{AlF}_3$  comparing that of  $\text{Al}_2\text{O}_3$  [12]. Cl-containing plasmas such as  $\text{BCl}_3$ ,  $\text{CCl}_4$ , and  $\text{SiCl}_4$  were also used to etch sapphire. In fact,  $\text{BCl}_3$ ,  $\text{CCl}_4$ , and  $\text{SiCl}_4$  have been used in the aluminum etching to remove native oxide( $\text{Al}_2\text{O}_3$ ) on the aluminum surface by forming volatile reaction species such as  $\text{BOCl}_x$  [13,14].  $\text{BCl}_3/\text{Cl}_2$  and  $\text{BCl}_3/\text{Cl}_2/\text{Ar}$  are well known gas combinations in the aluminum etching and also have been reported as the gas combinations with high etch rates achievable in the sapphire etching [10]. However, photoresist(PR) has much higher etch rates than sapphire. Therefore, to obtain more anisotropic etch profiles using photoresist, gas combinations that have higher etch selectivity over photoresist are required. In this study, sapphire etching was conducted in an inductively coupled plasma equipment using  $\text{BCl}_3$ -based gas combinations. The etch characteristics of sapphire were investigated in various etch conditions. To obtain high selectivities over photoresist and anisotropic etch profiles,  $\text{HBr}$  was used as an additive gas. Generally, hydrogen-containing halogen gases are used to obtain the high selectivity over photoresist and vertical profile in silicon etch processing [15,16].

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### II. EXPERIMENT

In this study, 2-inch diameter sapphire wafers with (0001) orientation were used as the etch samples. AZ 9260 photoresist (PR) was used as the etch mask, and 24  $\mu\text{m}$  thick PR was obtained by applying a double PR spin-on technique. Sapphire etching was performed in an inductively coupled plasma etcher. The substrate was maintained at 3  $^{\circ}\text{C}$  during the etching to prevent photoresist from reticulating.  $\text{Cl}_2$  and HBr were used as the additive gases to  $\text{BCl}_3$ , and the effect of these additive gases on the sapphire etch characteristics were investigated as a function of  $\text{Cl}_2$  and HBr. Throughout the experiment, the total gas flow rate, working pressure, inductive power, and dc bias voltage were maintained at 100 sccm, 12 mTorr, 1200 Watts, and -350 Volts, respectively. To analyze plasma characteristics which affect the etch process, optical emission intensities from  $\text{BCl}_3/\text{Cl}_2$  and  $\text{BCl}_3/\text{HBr}$  plasmas were monitored in-situ by optical emission spectroscopy (OES: SC Tech. PCM402) and ion saturation currents were measured by a Langmuir probe (Hiden Inc. ESP). The etch characteristics were investigated as a function of inductive power and dc bias voltage using 90 %  $\text{BCl}_3/10$  % HBr gas combination. In addition, to increase ion bombardment effect, 10 % of Ar gas was added to the gas combination. The total gas flow rate was maintained at 100 sccm and the working pressure at 10 mTorr. Inductive power and dc bias voltage to the substrate were varied from 600 to 1600 Watts and from -400 to -800 Volts, respectively. The etch rates were measured using a depth profilometer (alpha-step 500, TENCO). Especially, to observed the relation between dc bias voltage and etch profile angle, the etch profiles were inspected using a scanning electron microscope (SEM, Hitachi Inc. S-2150).

### III. RESULTS AND DISCUSSION

#### 1. Additive gas effect

Figure 1 shows the etch rates of sapphire and etch selectivities over PR in  $\text{BCl}_3/\text{Cl}_2$  and  $\text{BCl}_3/\text{HBr}$  plasmas. As shown in the figure, when 10-30 % of  $\text{Cl}_2$  or HBr were added to  $\text{BCl}_3$ , sapphire etch rates were close to or higher than that by  $\text{BCl}_3$  alone. In  $\text{BCl}_3/\text{Cl}_2$  gas combinations, sapphire etch rates were slightly increased with increasing  $\text{Cl}_2$  up to 20-30 and the highest sapphire etch rate in these conditions was about 3800  $\text{\AA}/\text{min}$ . However, the further increase of  $\text{Cl}_2$  in the  $\text{BCl}_3/\text{Cl}_2$  gas mixtures decreased the etch rates rapidly. In  $\text{BCl}_3/\text{HBr}$  gas combinations, sapphire etch rates were almost linearly decreased with HBr by adding more than 10 % in the gas mixture. The etch selectivities over PR were decreased with the increase of  $\text{Cl}_2$  and HBr. However, in  $\text{BCl}_3/\text{HBr}$  gas mixtures, etch selectivities over PR of about 0.9 could be obtained and these etch selectivities were comparatively higher than those by  $\text{BCl}_3/\text{Cl}_2$  gas combinations.

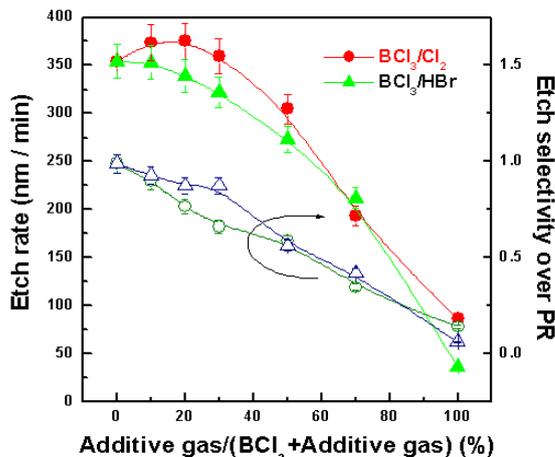


Fig. 1. Etch rates of sapphire and etch selectivities over PR for various  $\text{BCl}_3/\text{Cl}_2$  and  $\text{BCl}_3/\text{HBr}$  gas combinations.

Figure 2 shows optical emission intensities of ions and radicals measured by OES and ion saturation currents by a Langmuir probe during the sapphire etching. Figure 2(a) and (b) are shown for  $\text{BCl}_3/\text{Cl}_2$  and  $\text{BCl}_3/\text{HBr}$  plasmas respectively, and the monitored emission peaks were  $\text{BCl}$ (272.0 nm),  $\text{Cl}$ (754.7 nm),  $\text{H}$ (656.5 nm),  $\text{HBr}^+$ (358.1 nm), and chlorine ions( $\text{Cl}^+$ : 384.4, 385.1, 386.1 nm,  $\text{Cl}_2^+$ : 430.0 nm). As shown in the figure, with increasing HBr,  $\text{BCl}$  radical intensities decreased monotonically. However, the addition and increase of  $\text{Cl}_2$  to  $\text{BCl}_3$  up to 50 % increased  $\text{BCl}$  radical intensities and the further increase of  $\text{Cl}_2$  decreased  $\text{BCl}$  radical intensities rapidly. In the case of ion saturation current measured by a Langmuir probe, the increase of  $\text{Cl}_2$  and HBr to  $\text{BCl}_3$  increased the ion saturation currents monotonically. Also, the increase of optical emission intensities of the ions with additive gases such as the increase of  $\text{Cl}_2^+$  and  $\text{Cl}^+$  for  $\text{BCl}_3/\text{Cl}_2$  and the increase of  $\text{HBr}^+$  for  $\text{BCl}_3/\text{HBr}$  observed similar to the results on the ion saturation currents. In addition, with the increase of additive gases to  $\text{BCl}_3$ , chlorine radical intensities show monotonous increase for  $\text{BCl}_3/\text{Cl}_2$  and show monotonous decrease for  $\text{BCl}_3/\text{HBr}$ . If the results on the plasma characteristics were compared with sapphire etch rates shown in Figure 1, the variation of sapphire etch rates with increase of  $\text{Cl}_2$  and HBr appeared to be related to the abundance of  $\text{BCl}$  radicals in the plasmas. In general,  $\text{BCl}$  is known as the oxygen scavenger in aluminum etching in removing native aluminum oxide on the aluminum surface. Also, the results of ion saturation currents and ion emission intensities showed that the increase of ion bombardment with the increase of additive gases appears not to be effective in increasing sapphire etch rates possibly due to the sufficient ion bombardment in activating sapphire surface for the investigated conditions. Also, the variation of chlorine radicals with additive gases did not af-

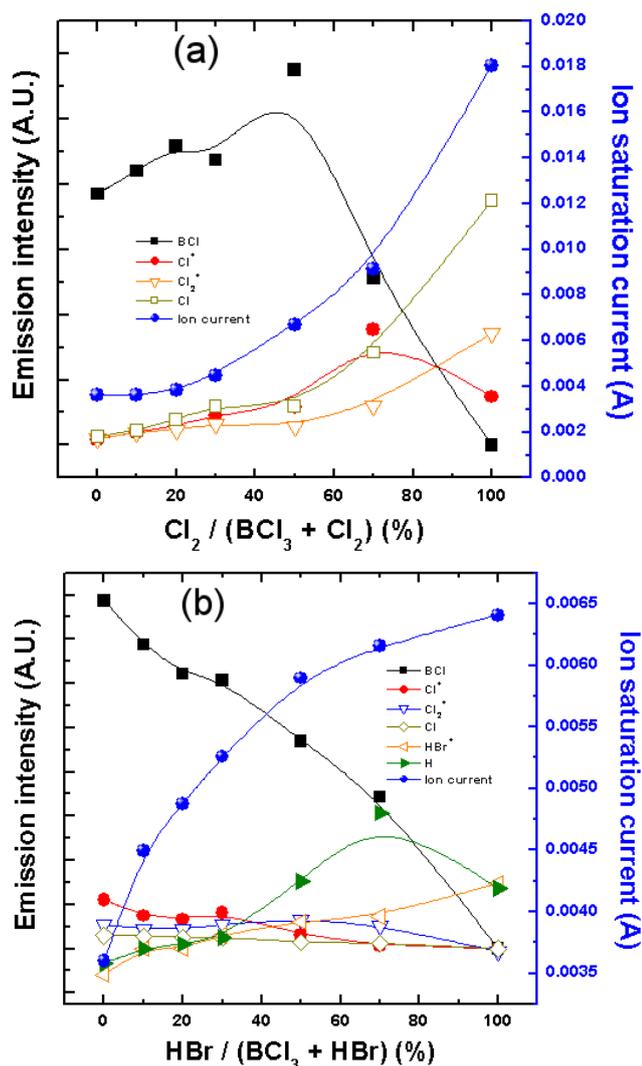


Fig. 2. (a)Optical emission intensities measured by OES and ion saturation currents measured by a Langmuir probe for various  $\text{BCl}_3/\text{Cl}_2$  gas combination. (b)Optical emission intensities measured by OES and ion saturation currents measured by a Langmuir probe for various  $\text{BCl}_3/\text{HBr}$  gas combination.

fect the sapphire etch rates significantly but increased the photoresist etch rates, therefore, decreased the etch selectivity.

## 2. Inductive power and dc bias voltage effect

From the above experimental results on the additive gas effect, relatively high selective sapphire etching could be obtained in the 90 %  $\text{BCl}_3/10$  %  $\text{HBr}$  gas combination. In our previous works, the sapphire etching in Ar added  $\text{BCl}_3/\text{HBr}$  and  $\text{BCl}_3/\text{Cl}_2$  gas combinations showed the highest sapphire etch rates in  $\text{BCl}_3/\text{HBr}$  and  $\text{BCl}_3/\text{Cl}_2$  gas combinations in low dc bias voltage conditions [12,

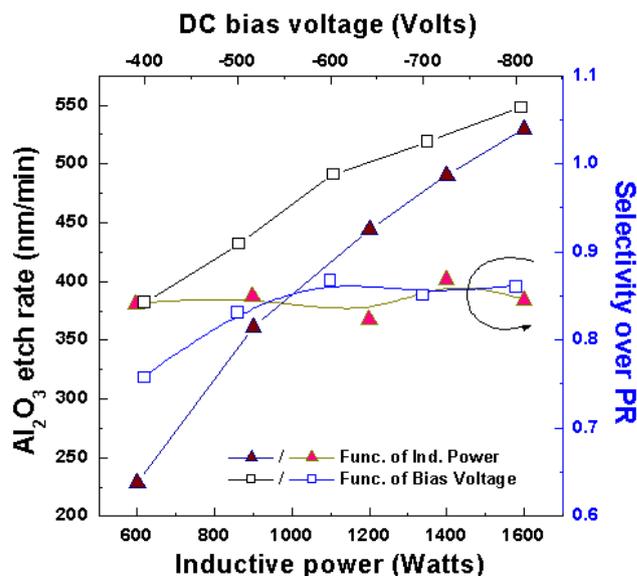


Fig. 3. Etch rates of sapphire and etch selectivity over PR as a function of dc bias voltage at 1400 Watts of inductive power and as a function of inductive power at -600 Volts.

13,17]. Therefore, in this study, the sapphire etching was performed in 10 % of Ar gas added 90 %  $\text{BCl}_3/10$  %  $\text{HBr}$  gas combination as a function of inductive power and dc bias voltage.

Figure 3 shows the sapphire etch rates as a function of inductive power at -600 Volts of dc bias voltage and as a function of dc bias voltage at 1400 Watts of inductive power. The inductive power was varied from 600 to 1600 Watts and dc bias voltages from -400 to -800 Volts. In the figure, the measured etch selectivities over photoresist are also shown. With the increase of inductive power from 600 to 1600 Watts, the etch rates of sapphire and photoresist were increased almost linearly. Therefore, the etch selectivities showed similar values near 0.85 for all of the investigated inductive power conditions. The etch rates of sapphire and photoresist were also increased with increasing dc bias voltage. However, at the low bias voltages up to -600 Volts, the increase of sapphire etch rate was faster than that of photoresist etch rate. Therefore, as shown in the figure, the etch selectivity was increased up to -600 Volts of dc bias voltage, however, at the higher dc bias voltages, the increase of sapphire etch rate and photoresist etch rate were similar, therefore, the etch selectivities were maintained nearly 0.85. In general, the increase of dc bias voltage increases the energy of ions and the increase of inductive power increases the flux of ions and radicals. Therefore, the increase of etch selectivity with increasing dc bias voltage at lower dc bias voltages is believed to be from the more sensitive sapphire etching with ion bombardment than photoresist etching. In this low dc bias voltage regime, the sapphire etch rate appears to be controlled by the sputter removal of the substrate material and less volatile reac-

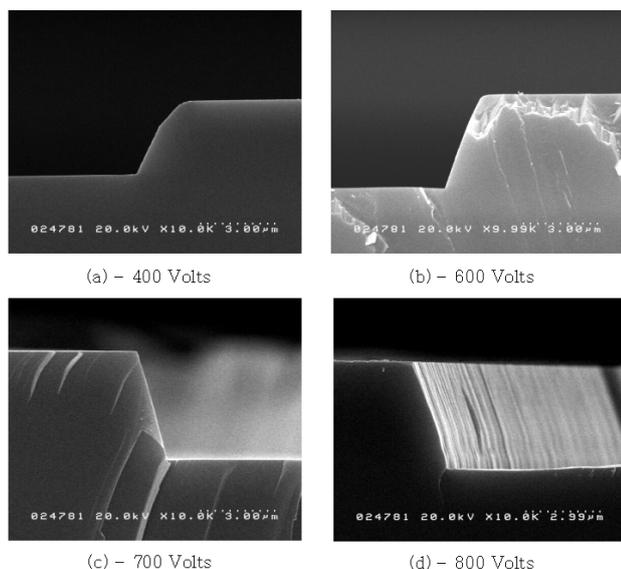


Fig. 4. Etch profiles of photoresist masked sapphire as a function of dc bias voltage at 1400 Watts of inductive power. Remaining photoresist was stripped off. (Process condition : 100 sccm of total flow rate, 10 mTorr of working pressure, 3 °C of substrate temperature, and 90 %  $\text{BCl}_3$ /10 % HBr mixed with 10 % Ar)

tion products formed on the sapphire surface. Also, from the above results, it is believed that the increase of sapphire etch rate with inductive power was not only due to the increase of ion bombarding species such as  $\text{BCl}_x^+$ ,  $\text{Cl}_x^+$ ,  $\text{Ar}^+$ , etc. but also due to the increase of reactive radical species such as  $\text{BCl}$ ,  $\text{Cl}$ ,  $\text{Br}$ , etc. On the other hand, the linear increase of sapphire etch rate with dc bias voltage shows that the bond breaking of Al-O by ion bombarding is still one of the important factors in the sapphire etching.

The highest sapphire etch rate obtained in the experiment was about 550 nm/min at -800 Volts of dc bias voltage and 1400 Watts of inductive power. The etch selectivity over photoresist at this condition was about 0.87. Even though the etch selectivity appeared to be saturated at high bias voltages and high inductive powers, the sapphire etch rate increased continuously with dc bias voltage and inductive power for the investigated conditions, therefore, higher sapphire etch rate appeared to be possible than that obtained in our experiment. Figure 4 shows the observed etch profiles of sapphire as a function of dc bias voltage at 1400 Watts of inductive power. The etch mask was 24  $\mu\text{m}$  thick photoresist, and remaining photoresist was stripped off before taking the pictures. The increase of inductive power did not change the etch profile significantly (not shown), however, the increase of dc bias voltage improved the etch profile more anisotropically as shown in the figure. If the results on etch selectivities in Figure 3 were compared with the sapphire etch profile angles in Figure 4, the etch profile an-

gles appeared to be related to the etch selectivity. Also, in addition to the higher etch selectivity over photoresist at higher dc bias voltages, the removal of etch products accumulated at the sidewall of the photoresist and etched structure by enhanced sputtering at the higher dc bias voltage appeared to assist to improve the etch profile. The highest etch profile angle was about 75 degree with the etch rate of 550 nm/min and etch selectivity of 0.87.

#### IV. CONCLUSIONS

In this study,  $\text{BCl}_3$  based inductively coupled plasmas were used to investigate the etch characteristics of photoresist patterned sapphire wafers as a function of additive gases such as  $\text{Cl}_2$  and HBr. Also, the effect of inductive power and dc bias voltage on the sapphire etching were investigated for a  $\text{BCl}_3$ /HBr gas mixture with 10 % Ar. The comparison of the results of the measured optical emission intensities by OES and the results of the sapphire etch rates showed that the sapphire etch rates appeared to be controlled by the abundance of  $\text{BCl}$  radicals in the plasma. Using 80 %  $\text{BCl}_3$ /20 %  $\text{Cl}_2$  gas chemistry, the highest sapphire etch rate of 380 nm/min could be obtained at a fixed inductive power and dc bias voltage. Using 90 %  $\text{BCl}_3$ /10 % HBr, the highest etch selectivities over photoresist of 0.9 could be obtained. Using the 90 %  $\text{BCl}_3$ /10 % HBr gas combination mixed with 10 % Ar, the effects of the inductive power and dc bias voltage on the sapphire etch characteristics were investigated. The increase of inductive power and dc bias voltage increased the sapphire and photoresist etch rates almost linearly. The etch selectivity over photoresist was remained similar for the investigated range of inductive power and dc bias voltage except for the low dc bias voltages. The highest sapphire etch rate obtained in the  $\text{BCl}_3$ /HBr/Ar plasma was 550 nm/min with the etch selectivity over photoresist about 0.87 and the anisotropic etch profile angle of 75 degree at 1400 Watts of inductive power and -800 Volts of dc bias voltage. Even though the etch selectivity appeared to be saturated at high bias voltages and high inductive powers, the sapphire etch rate increased continuously with dc bias voltage and inductive power for the investigated conditions, therefore, higher sapphire etch rates appear to be possible than that obtained in our experiment.

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## REFERENCES

- [1] Ch. Taschner, B. Ljungberg, V. Alfredsson, I Endler and A. Leonhardt, *Surf. Coat. Technol.* **108-109**, 257 (1998).
- [2] Y. dianran, H. Jining, W. Jianjun, Q. Wanqi and M. Jing, *Surf. Coat. Technol.* **89**, 191 (1997).
- [3] Y. H. Song, J.-H. Kim, H. J. Jang, S. R. Joon, J. W. Yang, K. Y. Lim and G. M. Yang, *J. Korean Phys. Soc.* **38**, 242 (2001)
- [4] D. J. Fu, Sh. U. Yuldashev, Y. H. Kwon, N. H. Kim, S. H. Park and T. W. Kang, *J. Korean Phys. Soc.* **39**, S313 (2001).
- [5] H. S. Na, H. J. Kim, S. Y. Kwon, E. J. Yoon, Y. B. Moon and M. H. Kim, *J. Korean Phys. Soc.* **37**, 971 (2000).
- [6] R. Kimura and K. Takahashi, *Jpn. J. Appl. Phys.* **39** 1039 (2000).
- [7] S. I. Dolgaev, A. A. Lyalin, A. V. Simakin and G. A. Shafeev, *Appl. Surf. Sci.* **96-98**, 491 (1996).
- [8] S. I. Dolgaev, A. A. Lyalin, A. V. Simakin, V. V. Voronov and G. A. Shafeev, *Appl. Surf. Sci.* **109-110**, 201 (1996).
- [9] X. Dongzhu, Z. Dezhang, P. Haochang, X. Hongjie and R. Zongxin, *J. Phys. D: Appl. Phys.* **31**, 1647 (1998).
- [10] Y. J. Sung, H. S. Kim, Y. H. Lee, J. W. Lee, S. H. Chae, Y. J. Park and G. Y. Yeom, *Mat. Sci. Eng. B* **82**, 50 (2001).
- [11] J. Kim, Y. Kim and W. Lee, *J. Appl. Phys.* **78**, 2045 (1995).
- [12] R. Hsiao, *IBM J. Res. & Dev.* **43**, 1/2 (1999)
- [13] A. J. van Roosmalen, J. A. G. Baggerman and S. J. H. Brader, Plenum Press, New York 116 (1991).
- [14] H. Kazumi, R. Hamasaki and K. Tago, *Jpn. J. Appl. Phys.* **36**, 4829 (1997).
- [15] S. Tabara, *Jpn. J. Phys.* **37**, 3570 (1998).
- [16] M. A. Vyvoda, H. Lee, M. V. Malyshev, F. P. Klemens, M. Cerullo, V. M. Donnelly, D. B. Graves, A. Kornblit and J. T. C. Lee, *J. Vac. Sci. Technol. A* **16**, Nov/Dec 3247 (1998).
- [17] C. H. Jeong, D. W. Kim, K. N. Kim and G. Y. Yeom, *Jpn. J. Appl. Phys. Part1* **41**, 6202 (2002).