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PROCESSING OF $PbTiO_3$ AND $Pb(Zr_xTi_{1-x})O_3$ THIN FILMS BY NOVEL SINGLE-SOLID-SOURCE METALORGANIC CHEMICAL VAPOR DEPOSITION

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ABSTRACT

Ferroelectric $PbTiO_3$ (PT) and $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films have been deposited on (100) MgO and (111) $Pt/SiO_2/(100)Si$ substrates by using a novel single-solid-source metalorganic chemical vapor deposition (MOCVD) technique. The new technique uses a powder delivery system to deliver the mixed precursor powders directly into a hot vaporizer from room temperature, therefore, avoiding any problems associated with polymerization or decomposition of the precursors before evaporation. The technique simplifies MOCVD processing significantly and can improve process reliability and reproducibility. The deposited PT and PZT films have a perovskite structure and are highly oriented with respect to the substrate. With improvement of process control, systematic studies of film evolution under various growth conditions have been carried out. Effects of substrate, substrate temperature, system vacuum, and precursor ratios in the mixture on film microstructure and properties will be presented in this paper.

INTRODUCTION

Potential applications of ferroelectric lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films in electronic and optical devices, such as non-volatile high-speed ferroelectric random access memories (FRAMS), optical storage discs, piezoelectric actuators and pyroelectric detectors, have led to extensive study on the processing of the thin films[1-4].

Among various thin film deposition techniques, metalorganic chemical vapor deposition(MOCVD) process offers, in principle, many advantages, such as excellent film uniformity and homogeneity, easy component control, high deposition rate, conformal deposition and feasibility for large-scale processing. In a typical MOCVD process, metalorganic precursors for each element are vaporized in separate bubblers and carried to growth chamber by individual gas delivery lines. MOCVD has been used to deposit PZT films by a number of groups[5-11]. Solid metalorganic precursors, such as β-diketonate compounds, $Pb(thd)_2$ and $Zr(thd)_4$ (thd=2,2,6,6-tetramethyl-3-5-heptanedionate), are preferred in the depositions because they are non-toxic as compared with liquid precursors such as tetraethyllead $Pb(C_2H_5)_4$ (TEL) which is extremely toxic. The problems currently limiting commercial applications of MOCVD for growing the oxide thin films are poor reliability and reproducibility due to inconsistencies in the transport of the metalorganic precursors to the substrate[12-15]. In order to have sufficiently high vapor pressure for deposition, the precursors often have to be heated to a relatively high temperature, typically near the melting temperature of the precursor (if the precursor is solid powder), at which point the precursors could start to polymerize or decompose or simply agglomerate. As a result, the vapor pressures of precursors decay over the repeated thermal cycles, causing difficulties in composition control. Temperature fluctuation along the vapor delivery line also causes additional instability in precursor transport due to either decomposition or condensation of the precursor along the line.

In order to improve the system control of MOCVD for deposition of complex oxide materials, single-source MOCVD systems have been developed in recent years[13-16]. We have developed a novel MOCVD system based on single-solid-source[17,18]. The new technique uses a powder delivery system to deliver the mixed precursor powders directly from room temperature into a hot vaporizer where the precursors are evaporated simultaneously and are carried into deposition chamber. The technique simplifies MOCVD processing significantly and improves

process control. In this paper, growth characteristics of PT and PZT films deposited on (100) MgO and (111) Pt/SiO_2/(100)Si substrates by the MOCVD will be reported. Effects of substrate, substrate temperature, system vacuum pressure, precursor ratios in the mixture on film microstructure and properties are systematically investigated.

EXPERIMENTAL

Details of the novel single-solid-source MOCVD have been reported elsewhere[17]. In brief, the technique employs a single-solid-source delivery system to deliver pre-mixed solid powders of the precursors at room temperature directly into a vaporizer maintained at a high temperature, where all precursors evaporate simultaneously and are carried into deposition chamber by a carrier gas. Fig.1 shows a schematic diagram for the powder delivery system[17]. The uniformly mixed solid powders of the precursors are pressed into a cylinder of diameter of about 3 mm. The cylinder is driven through a quartz tube from one end, by a precision screw drive. At the other end of the quartz tube, a mini-motor with rotating blades is used to gently break the pressed cylinder into powder. The powder drops, mainly due to gravitation, through a stainless-steel tube to a vaporizer. The stainless-steel is cooled by a water jacket. Since the powders drop through the stainless-tube from the end of quartz tube at room temperature to the vaporizer at high temperature in less than 0.1 second (the time it takes for the powders to drop about 5 cm due to gravitation), in effect, an extremely large temperature gradient is created. Therefore, any problems due to polymerization or decomposition of the precursors in the near hot zone are avoided. The uniform delivery of the powders to the vaporizer is achieved as long as the speed of precision screw drive is constant. The speed of the drive can be controlled to be as slow as 10^{-2} mm/min, which corresponds to the smallest delivery rate of about 10^{-5} gm/min.

The PT and PZT thin film depositions were carried out in a low pressure, horizontal, cold wall reactor with a resistive substrate heater. N_2 was used as the carrier gas for the vapor. O_2 was delivered directly to the reaction chamber. The substrates used for deposition included (100) MgO, and (111) Pt/SiO_2/(100)Si. Commercially pure β-diketonate complexes, $Pb(thd)_2$, $Zr(thd)_4$ and $OTi(thd)_2$, which are all dry powders, were used as Pb, Zr and Ti precursors, respectively, for the PZT deposition. Film composition was controlled by varying the molar ratio of the precursors in the powder mixtures. The vaporizer temperature is maintained at 290°C. Typical system pressure is about 6 torr. The substrate temperarure varies between 500-700°C. The deposition rates were controlled at 4-10nm/min. The typical film thickness was 0.3-0.5 microns. PZT film compositions were obtained by energy dispersive x-ray spectroscopy (EDS) in a scanning electron microscope(SEM). The crystalline structure of the films was characterized by x-ray diffraction(XRD) using Cu K_α radiation.

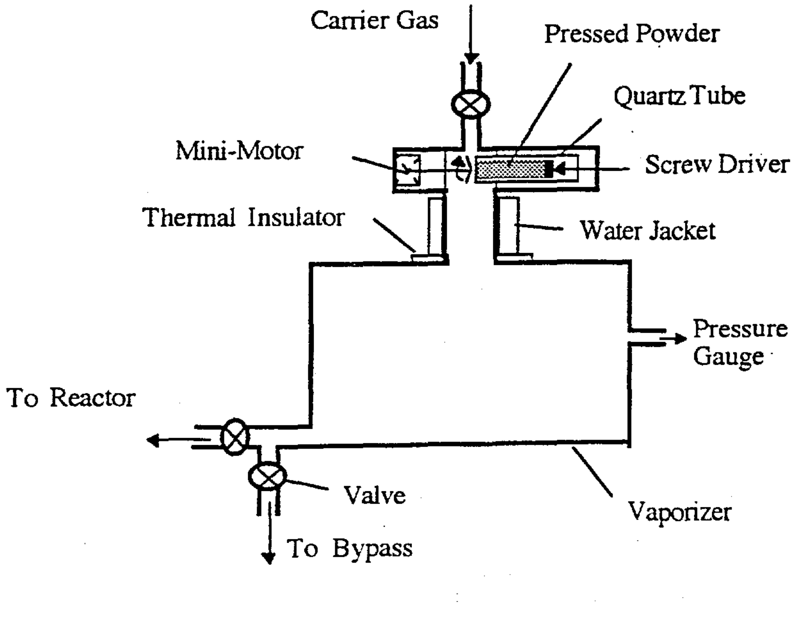

Fig.1. Schematic diagram showing the single-solid-source delivery system.

RESULTS AND DISCUSSION

Film composition was controlled by varying molar ratio of the precursors in the powder mixture. The proper ratios in the powder mixture required for deposition of stoichiometric PT and PZT films were found to be dependent on the substrate temperature and substrate. Fig.2 shows the relationship between the required Pb/Ti molar ratios in the powder mixture, substrate temperature and substrates, for deposition of stoichiometric PT. The Pb/Ti molar ratio in the mixture, required for the stoichiometric deposition, increases with increasing deposition temperature. For the PT films on the MgO, the proper Pb/Ti ratio is about 0.47 at a substrate temperature of 600°C, and about 0.56 at a substrate temperature of 650°C. The films deposited at these ratio are highly oriented with its [001] and [100] axis perpendicular to the substrate surface[17]. The higher content of Pb precursor required at a higher temperature is perhaps due to the increased desorption rate of the Pb at the higher temperature.

Films deposited on the Pt under the same conditions to those on the MgO were off-stoichiometric and undesirable. Deposition of the films on the Pt substrate requires a higher Pb/Ti molar ratio in the precursor mixture than that needed for the films on the MgO substrates under identical conditions. As shown in Fig.2, the proper Pb/Ti ratios are about 0.58 and 0.73 at substrate temperatures of 600°C and 650°C, respectively, for the PT films on the (111) Pt/SiO$_2$/(100) Si substrate. The x-ray patterns of the PT films deposited at these conditions are shown in Figs.3a and 3b, respectively. Different deposition characteristics observed on the Pt and MgO substrates are perhaps due to different absorption, reaction and desorption properties of the precursors on the two substrates.

A similar temperature dependence is also observed for the PZT films. The films deposited at a higher substrate temperature requires a higher Pb/(Ti+Zr) molar ratio in the mixture. The proper ratios required for PZT deposition is also strongly dependent on the substrates. The Zr composition in the films can be increased gradually as the Zr/(Ti+Zr) molar ratio in the powder mixture increases. Fig.4 shows a non-linear relationship observed between the Zr composition and the Zr/(Zr+Ti) ratio for the films deposited on MgO at 675°C. This relationship is similar to the relationship reported for PZT deposition using different precursors[10]. The relationship

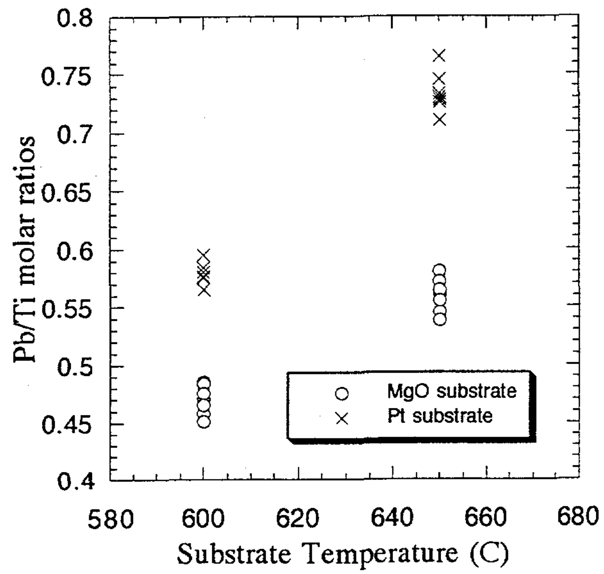

Fig.2. The Pb/Ti ratios required for stoichiometric PT deposition as a function of substrate and substrate temperature.

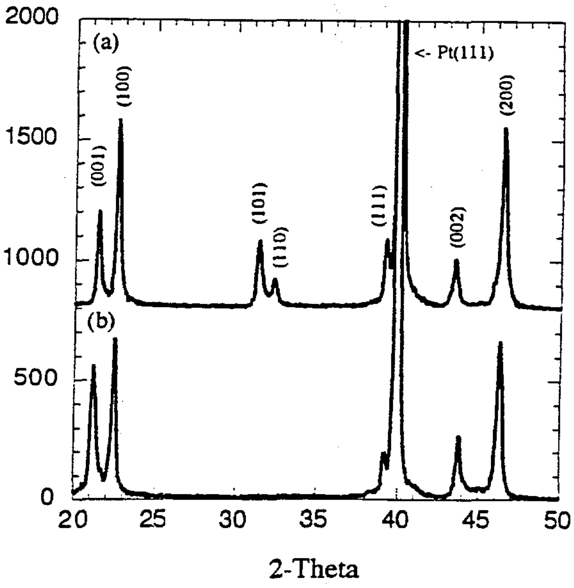

Fig.3. XRD patternd of PT films grow on the Pt substrate under conditons: (a) 600°C and Pb/Ti molar ratio of about 0.58; and (b) 650°C and Pb/Ti molar ratio of about 0.73.

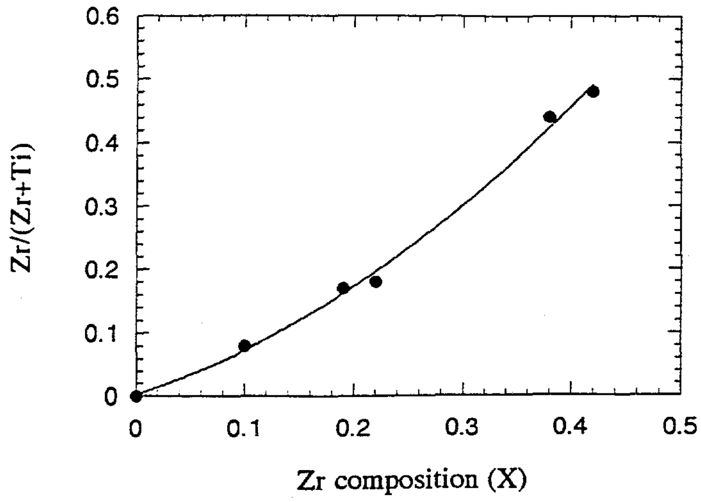

Fig.4. Dependence of Zr composition (x) on the Zr/(Zr+Ti) molar ratio in the powder mixture for the PZT films deposited on (100) MgO substrate at 675°C.

indicates that the excess Zr in the gas phase, e.g. the Zr/Ti molar ratio in the gas phase higher than the stoichiometric value in the films, is needed for the PZT deposition. This result can be explained based on the difference in the rate of reaction between the PbO with TiO_2, and the PbO with ZrO_2. The reaction rate of PbO with TiO_2 was reported to be much higher than that of PbO with ZrO_2[19]. The Zr composition was limited to about 0.4 for the PZT films deposited on the MgO substrate and about 0.2 for the PZT films deposited on the Pt substrate directly. A higher Zr/(Ti+Zr) ratio in the powder mixture often leads to the films deposited along with ZrO_2 and the Zr related particles, and the films with poor surface morphology. Similar difficulties in deposition of high Zr composition PZT films have been also reported before and were attributed to formation of pyrochlore and ZrO_2 phase on the substrate with the increase of Zr in the gas phase[20-22].

Deposition of PZT films with a higher Zr composition on the Pt substrate was achieved by using a two-step growth process[18]. In the two-step process, a thin PT buffer layer about 10nm was deposited on the Pt substrate first, and was followed by deposition relatively thick PZT films on top of the PT buffer layer. Using the process, PZT films with Zr contents up to about 40 mol% can be deposited. The non-linear relationship similar to that in Fig.4 was also observed for PZT films deposited on the PT buffer layer. The x-ray patterns of PZT films deposited at 675°C with the Pb/Ti molar ratio of 1.20 and the Zr/(Ti+Zr) molar ratio of 0.20, 0.50, and 0.62, are shown in Figs. 5a, 5b and 5c, respectively. The films in Figs.5a and 5b have a Zr composition of about 0.2 and 0.4, respectively, based on the splitting observed between (001) and (100) peaks in the x-ray pattern. Attempts at further increasing Zr composition again lead to formation of ZrO_2 and related phases on the PT buffer layer and resulted in the PZT films with very poor surface morphology. The film deposited with the Zr/(Zr+Ti) ratio of 0.62 in Fig.5c, has a broad peak in the x-ray pattern at about 34.4°, corresponding to monoclinic ZrO_2 (020) reflection, in addition to the PZT peaks.

System pressure was found to have considerable effect on the PZT films deposited by the two-step process. Figs.6a, 6b and 6c show the x-ray patterns of the PZT films grown at system pressure of 6 torr, 15 torr and 30 torr, respectively. The films were deposited at 675°C with a Pb/Ti molar ratio of 1.15 and a Zr/(Zr+Ti) molar ratio of 0.22. As shown in Fig.6, the (100) and (001) or (200) and (002) peak splitting decreases gradually as the system pressure is increased, indicating that high system pressure enhances the Zr content in the films. The morphology of the films, however, degrades rapidly with increasing system pressure. Film inhomogeneities were the largest for the highest pressure studied of 30 torr.

CONCLUSIONS

A novel single-solid-source MOCVD technique has been used to deposit ferroelectric PT and PZT thin films on (100) MgO and (111) Pt/SiO_2/(100)Si substrates. The new technique, which uses a powder delivery system to deliver the mixed precursor powders directly into a hot vaporizer from room temperature, simplifies MOCVD processing and improves process control. Systematic studies of effects on the film growth by substrate, substrate temperature, system vacuum pressure, precursor molar ratios in gas phase have been carried out. It was found that growth behavior of PT and PZT films is substrate and substrate temperature dependent. For stoichiometric deposition, different precursor ratios in the gas phase are required for different substrates and substrate temperatures. The excess Zr is needed in the gas phase for PZT deposition. Deposition of PZT with a high Zr composition (x>0.4) using the precursors in the study is often associated with precipitation of ZrO_2 and related particles in the films and degradation of film surface morphology. Deposition of the PT buffer layer on the Pt coated substrates is very beneficial for formation of perovskite PZT films. Higher system pressure helps incorporation of Zr into the PZT film but reduces the film homogeneity.

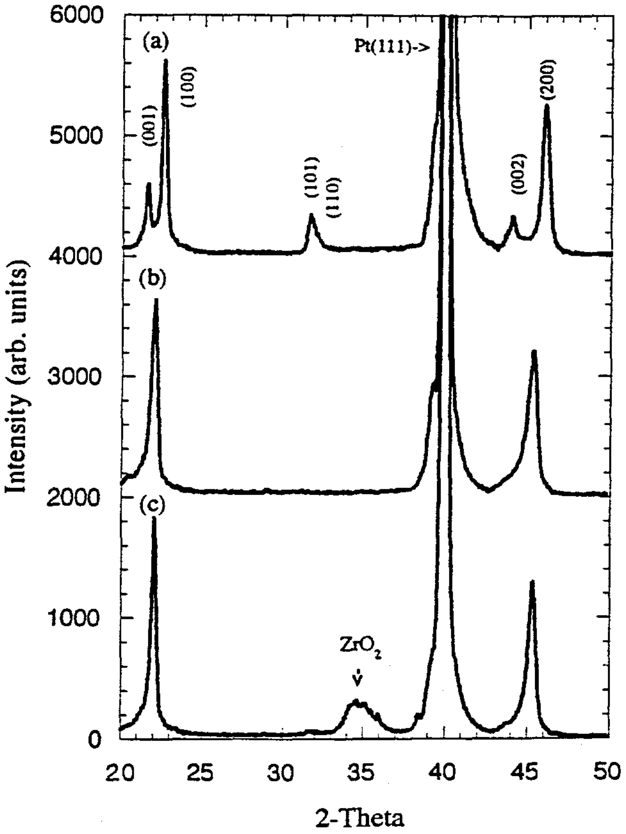

Fig.5. XRD patterns of PZT films grown by two-step process at 675°C with the Pb/Ti molar ratio of 1.20 and Zr/(Zr+Ti) molar ratio of (a) 0.20, (b) 0.50 and (c) 0.62, respectively.

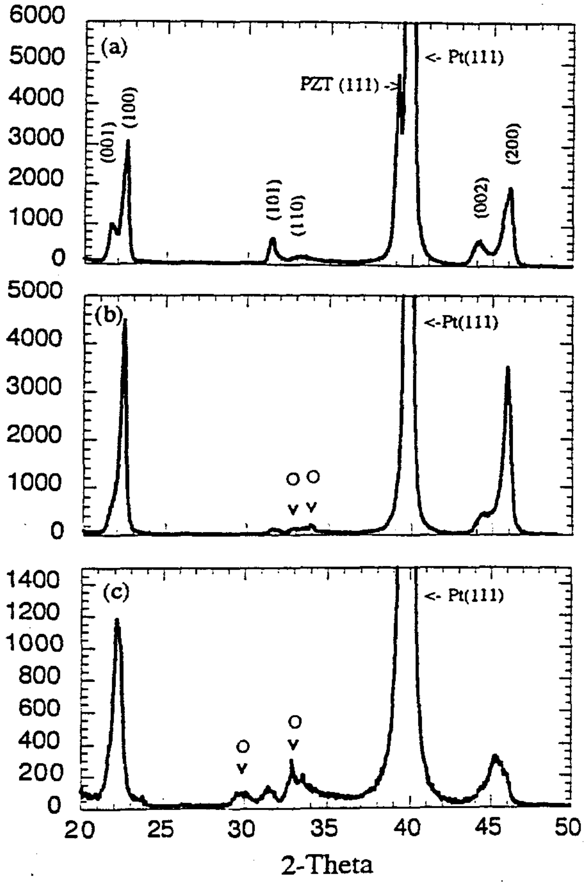

Fig.6. XRD patterns of PZT films grown by two-step process at 675°C with system pressure of (a) 6 torr, (b) 15 torr and (c) 30 torr, respectively.

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REFERENCES

[1] See for instance, Epitaxial oxide thin films II (Mrs. Res. Soc. Symp. Proc. 401), Edited by J.S. Speck, D.K.Fork, R. M.Wolf and T. Shiosaki, (1996)

[2] J.F.Scott and C.A. Paz De Arauj, Science 246,1400 (1989).

[3] S.Sinharoy, H. Buhay, D.R.Lampe and M.H.Francombe, J. Vac. Sci. Technol. A10, 1554 (1992).

[4] G. H. Haertling, J. Vac. Sci. Technol. A9, 414 (1991).

[5] M. Okada, K. Tominaga, T.Araki, S. Katayama and Y. Sakashita, Jpn. J. Appl. Phys. 29, 718 (1990).

[6] Y. Sakashita, T. One, H. Segawa, K.Tominaga, M. Okada, J. Appl. Phys. 69, 8352 (1991).

[7] B.S. Kwak, E.P. Boyd and A.Erbil, Appl. Phys. Lett. 53, 1702 (1988).

[8] G.R. Bai, H.L. M.Chang, H.K. Kim, C.M.Foster, and D.J.Lam, Appl. Phys. Lett. 61, 408(1992).

[9] C. Peng and S. B. Desu, Appl. Phys. Lett. 61, 16 (1992).

[10] M. Shimizu and T. Shiosaki, Mat. Res. Soc. Symp. Proc. 361, 295 (1995).

[11] C.M. Foster, R. Csencsits, P. M. Baldo, G. R.Bai, Z. Li, L.E. Rehn, L. A. Wills, R. Hiskes, D. Dimos and M.B. Sinclair, Mat. Res. Soc. Symp. Proc. 361, 307 (1995).

[12] J.Zhao, C.S.Chern, Y.Q.Li, D.W.Noh, P.Norris, P.Zawadzki, B.Kear and B.Gallois, J. Crystal Growth 107, 699 (1991).

[13] R.Hiskes, S.A.DiCarolis, R.D. Jacowitz, Z.Lu, R.S. Feigelson, R.K.Route and J.L.Young, J. Crystal Growth 108, 781 (1993).

[14] R.Hiskes, S.A.DiCarolis, J.L.Young, S.S.Laderman, R.D. Jacowitz, and R.C. Taber, Appl. Phys. Lett. 59, 606 (1991).

[15] J.Zhang, R.A. Gardiner, P.S. Kirlin, R. W.Boerstler and J. Steinbeck, Appl. Phys. Lett. 61, 2884 (1992).

[16] P.S Kirlin, R.L. Binder and R.A. Gardiner, US Patent Application 07/807, 807.

[17] P. Lu, H. Li, S.Sun and B. Tuttle, J. Crystal Growth 171, 453 (1997).

[18] P. Lu, H. Li, S.Sun, Y. M. Wang and B. Tuttle, J. Crystal Growth, Submitted.

[19] G.R.Bai, H.L.M.Chang, D.J. Lam and Y. Gao, Appl. Phys. Lett. 62, 1754 (1993).

[20] M. Shimizu, M. Sugiyama, H. Fujisawa and T. Shiosaki, Jpn. J. Appl. Phys. 33, 5167 (1994).

[21] M. Shimizu, M. Fujimoto, T.Katayama, T. Shiosaki., K. Nakaya, M.Fukagawa and E. Tanikawa, Mater. Res. Soc. Symp. Proc. 310, 255 (1993).

[22] H. Tomonari, T. Ishiu, K. Sakata and T. Takenaka, Jpn. J. Appl. Phys. 31, 2998 (1992).

[23] I. Kanno, S. Hayashi, T. Kamada, M. Kitagawa and T. Hirao, Jpn. J. Appl. Phys. 32, 4057 (1993).