

Comparison between ZnO films grown by atomic layer deposition using H₂O or O₃ as oxidant

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Abstract

This study investigated the atomic layer deposition (ALD) behavior of zinc oxide (ZnO) films on SiO₂/Si substrates using Zn(C₂H₅)₂ and O₃ as the precursor and oxidant, respectively, at substrate temperatures ranging from 230 to 300 °C, and the electrical properties of the thin films. The self-limiting ALD mechanism of ZnO thin film growth was confirmed in the whole temperature region, and the growth rate decreased from 0.19 nm/cycle at 230 °C to 0.16 nm/cycle at 300 °C. ZnO films with a *c*-axis preferential orientation were obtained at these relatively low temperatures. The films contained a lower oxygen concentration compared to the films grown with the same precursor and H₂O oxidant. However, the ZnO film grown with the O₃ oxidant at 300 °C showed approximately a resistivity three orders of magnitude higher than that of the ZnO film using the H₂O oxidant, due to higher Si impurity concentration in the ZnO films. Si diffusion into the ZnO films must be due to the stronger oxidation power of O₃ compared to H₂O.

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1. Introduction

Zinc oxide (ZnO) is an *n*-type semiconductor material with a hexagonal wurzite structure and a band gap of 3.0 eV at room temperature. ZnO thin films have been grown for various thin-film-device applications, including gas sensors [1,2], surface acoustic wave (SAW) devices [3], transparent conducting electrodes for solar cells and displays [4,5]. Recently, there has been considerable interest in ZnO films for their application to short-wavelength optical devices including light emitting diodes and laser diodes, due to its high exciton binding energy (60 mV) [6].

ZnO thin films can be deposited by several deposition methods, such as chemical vapor deposition (CVD), reactive magnetron sputtering and electron-beam evaporation, etc. [7,8]. Recently, atomic layer deposition (ALD) [9],

which is capable of growing uniform high-quality thin films on a large area and on flexible substrates at low temperature, has been extensively studied for the ZnO thin film growth. In contrast to conventional CVD where the precursors and reactants are simultaneously injected into the chamber, ALD is a method based on the sequential introduction of the respective reaction precursors. ALD proceeds by specific surface ligand-exchange reactions and not by the thermal decomposition of the precursors. Therefore, layer-by-layer growth and a full or partial monolayer deposition per one alternative precursor injection can be obtained. Due to the self-limiting mechanism, thin films with high quality can be obtained with a precise thickness control and excellent conformality over severe three-dimensional surface structures.

The most commonly used precursor and oxidant for the ALD of ZnO thin films are diethylzinc Zn(C₂H₅)₂ (DEZ) and H₂O, due to their excellent self-limiting ALD mechanism. ALD using DEZ and H₂O resulted in the ZnO thin

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films with a preferential $\langle 100 \rangle$ growth direction parallel to the substrates' normal direction when the growth temperature (T_g) was < 200 °C. However, films with a $\langle 002 \rangle$ preferential growth direction were obtained when the T_g was > 300 °C [10]. It has also been reported that ZnO thin films with a $\langle 002 \rangle$ preferred growth direction were obtained at a T_g of 300 °C when an electric field was applied [11].

The required structural and electrical properties of the ZnO films depend on specific applications. For example, transparent conducting oxide applications require a lower resistivity and the $\langle 100 \rangle$ preferred growth direction of the films. However, SAW filter applications require ZnO films with a $\langle 002 \rangle$ preferred growth direction and a higher resistivity. Therefore, these films need to be grown at higher temperatures or be postannealed for their applications in fields where a high resistivity is necessary.

In this study, ZnO films were grown by the ALD process using DEZ and a high concentration of (400 g/m^3) O_3 as oxidant. The self-limiting growth behavior of the ALD process was confirmed, and the variations in the structural and electrical properties of the ZnO films were compared with the ZnO films grown by ALD using DEZ and H_2O .

2. Experimental procedure

A traveling wave-type ALD reactor (Ever-tek, Plus-100) was used for ZnO film growth. The vaporization temperature of the DEZ was 15 °C, and no carrier gas was used for the DEZ delivery. A 1000 standard cubic centimeter per min (sccm) $\text{O}_2/10$ sccm N_2 gas mixture was introduced into the O_3 generator, and an O_3 gas at a concentration of 400 g/m^3 was obtained. Ar gas (900 sccm) was used as purge gas. The DEZ injection times were varied between 0.1 and 2 s, and the O_3 injection time was fixed at 1 s. A rather long purge time (5 s for the DEZ and O_3 purges) was adopted in order to prevent precursor and oxidant mixing. Four-inch-diameter Si wafers with a 200-nm-thick SiO_2 layer were used as substrate. T_g , which was measured by a thermocouple wafer under the same pressure as the actual deposition runs, was varied from 170 to 300 °C. The schematic diagram of the ALD system is shown in Fig. 1. In our system, a by-pass line was used to maintain a uniform pressure during the

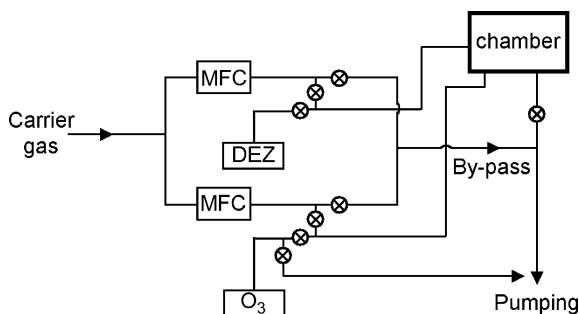


Fig. 1. Schematic diagram of the ALD system.

growth process; when a source was introduced into the ALD chamber, the purge gas, Ar, flowed through the by-pass line.

The film thickness was measured by ellipsometry and cross-section transmission electron microscopy (TEM). The preferred growth direction and crystal structure were examined by X-ray diffractometer in θ – 2θ mode with $\text{Cu-K}\alpha$ radiation and TEM. The film compositions (O/Zn ratio) of the films were qualitatively investigated by an Auger electron spectroscopy (AES) depth profile using an electron beam energy of 5 kV. Depth profiles of the films were examined by secondary ion mass spectrometry (SIMS). Secondary ions were detected using a Cs^+ primary ion beam with a beam current of 10 nA. The carrier-type, concentrations and electron mobility were measured using a Hall measurement with the Van der Pauw electrode configuration under a magnetic field of 0.5 T at room temperature. The surface roughness of the films was measured by atomic force microscopy (AFM) in noncontact mode with a tip constant of 40 N/m and resonance frequency of 300 kHz.

3. Results and discussion

Fig. 2 shows the variation in the film growth rate (thickness/cycle) as a function of the DEZ precursor injection time with a given O_3 injection time of 1 s at a T_g of 250 °C. The growth rate increased with increasing DEZ injection time up to 1 s and saturated to a 0.19 nm/cycle when the injection time was > 1 s. This confirms that a self-limiting ALD mechanism of ZnO thin film growth was obtained using DEZ and O_3 as the Zn precursor and oxidant, respectively. The saturated growth rate of 0.19 nm/cycle was similar to the ZnO film growth rate by ALD using DEZ and H_2O . It was reported that the growth rate in the ALD is determined by the geometries of the reacting molecules and the density of the adsorption sites on the surface [12]. If saturated adsorption prevails, the number of adsorbed atoms can be found by tightly packing the adsorbates on the surface sites. In particular, the growth rate in the ALD of oxide thin films is likely to be determined by the precursor rather than the oxidant because the precursor molecular size is usually larger than that of the oxidant molecules. Therefore, as long as DEZ is used as a precursor for the ZnO growth, the use of O_3 instead of H_2O as oxidant does not influence the growth rate.

Fig. 3 shows the variations in the saturated growth rate as a function of the deposition temperature when the oxidants were O_3 and H_2O , respectively. The T_g was varied from 170 to 300 °C for the O_3 oxidant case. However, film growth was not observed at $T_g < 230$ °C. The growth rate was invariant at T_g s between 230 and 250 °C but slightly decreased with increasing T_g when T_g was > 250 °C, probably due to the increased desorption of the DEZ molecules or oxidant functional groups from the growing surface. The same trend was observed in the case of the H_2O oxidant with an approximately 100 °C lower growth

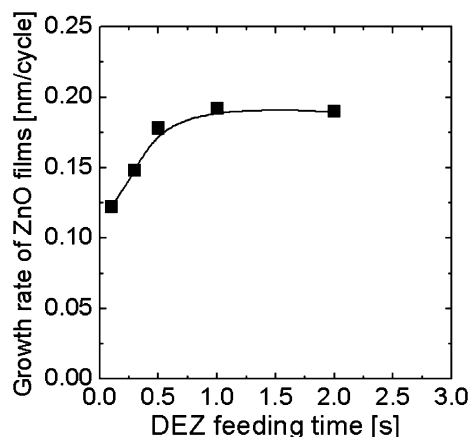


Fig. 2. The variation in the growth rate of ZnO films as a function of the DEZ feeding time at 250 °C.

temperature. ALD of ZnO film using DEZ and H_2O proceeds by donating two H^+ ions from two H_2O molecules to the C_2H_5 ligands of the DEZ molecules, resulting in the release of two C_2H_6 molecules and forming $\text{Zn}(\text{OH})_2$ species on the surface. However, it was believed that, for the case of O_3 , which is a very strong oxidant, the ALD reaction proceeds via the simple oxidation of the adsorbed DEZ molecules. It can be considered that the O_3 burns the hydrocarbon ligands and forms CO_2 and H_2O molecules. Then, the produced H_2O may play a major role in the ALD reaction. This theory, although, could not satisfactorily explain the results from our experiments because the burning out of the hydrocarbons by O_3 would locally increase the surface temperature. Then, if the produced H_2O plays the major role in the ZnO ALD, the process temperature region (the setting temperature) must be decreased. However, the ALD using O_3 actually took place in the higher temperature region, as shown by Fig. 3, which suggests that the ALD reaction was governed by some other mechanism than the usual OH^- group-mediated one. This may also indicate that the actual temperature increase by the burning reaction is not so serious. The following reaction mechanism was assumed for the O_3 -based-ALD process of ZnO films. CO_x and H_2O are produced by the reaction between the hydrocarbons and the input O_3 . Then, the produced Zn metal ion may react with either the produced H_2O to produce $\text{Zn}(\text{OH})_2$, or with the oxygen atoms or O_3 molecules to form ZnO. Because of the reason given above, it is believed that the direct oxidation of the Zn ions to ZnO dominates the $\text{Zn}(\text{OH})_2$ formation. During the next step of DEZ pulse, the DEZ molecules may react with the excess oxygen ions on the surface, or the Zn ions of the DEZ may directly bond chemically to the O ions of the grown ZnO film. In the next step, the residual hydrocarbon of the DEZ molecules are removed by O_3 . It seems that the kinetics for this reaction is faster than the ALD reaction by the produced H_2O . It seems that the oxidation of DEZ by O_3 requires a higher thermal energy, which means that O_3 -ALD requires a higher T_g . It should be noted that the higher process

temperature does not necessarily mean that the kinetics for this process is slower.

Since the ALD mechanism here is not similar to the H_2O -based one, the slower growth rate at higher temperatures ($>280^\circ\text{C}$) must be due to the less active adsorption of DEZ. Fig. 3 shows that the growth rate of the ZnO film using the H_2O oxidant was less than half of the growth rates at much lower temperatures, which must result from the increased desorption of either H_2O or DEZ. It is usually considered that the surface OH^- groups work as the anchoring sites for the metal ions during the next precursor pulse step. Therefore, the decreased growth rate at 280°C should most probably result from less adsorption of H_2O on the growing film surface. However, it was also found that, in the ALD of Al_2O_3 films using trimethylaluminum and H_2O , this sort of growth rate decrease at such a relatively low temperature could not be observed. Therefore, the less active adsorption of DEZ at this temperature cannot be ruled out as a reason for the lower growth rate. The decreasing growth rate at higher temperatures ($>280^\circ\text{C}$) for the O_3 -based ALD of ZnO film might also result from the increased desorption of DEZ at such a high temperature. O_3 -based ALD of ZnO films at even higher temperatures could not be performed because the DEZ begins to thermally decompose at such higher temperatures.

Fig. 4(a) shows the X-ray diffraction patterns of ZnO thin films grown at T_g s from 230 to 300°C , using the O_3 oxidant and (b) shows those of the films grown at T_g s of 170 and 230°C , using the H_2O oxidant. The ZnO thin films grown with the O_3 oxidant show a $\langle 002 \rangle$ direction preferred orientation [most of the grains have their (002) planes parallel to the substrate surface] in the whole T_g range. However, for the cases of ZnO films grown with H_2O as oxidant, the films grown at 170°C show a rather random orientation or a slightly $\langle 100 \rangle$ direction preferred growth behavior, whereas the film grown at 230°C shows a relatively $\langle 002 \rangle$ direction preferred growth behavior. It should be noted that the $\langle 002 \rangle$ direction of a ZnO film is

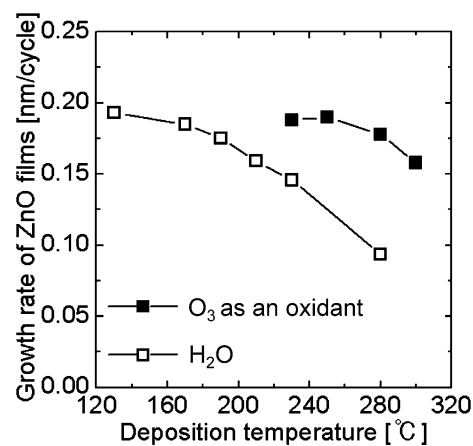


Fig. 3. The variations in the growth rate of ZnO films as a function of the deposition temperature for H_2O and O_3 oxidants, respectively.

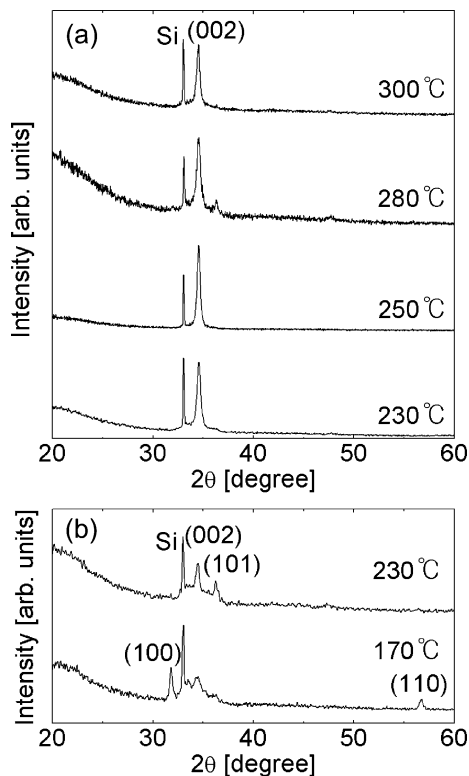


Fig. 4. X-ray diffraction pattern of the ZnO films as a function of the deposition temperature using an (a) O_3 and (b) H_2O oxidant.

the most thermodynamically favorable growth direction because of the low surface energy of the (002) plane. For the case of the ZnO ALD with H_2O as oxidant, the higher T_g results in a more preferred growth in the $\langle 002 \rangle$ direction because this is the thermodynamically favorable direction. In the case of the O_3 oxidant, the $\langle 002 \rangle$ preferred growth behavior also results from a higher T_g ($>230^\circ C$) with the help of the strong oxidation power of O_3 . ZnO films with a $\langle 002 \rangle$ preferred orientation are needed for SAW devices [3].

Fig. 5 shows the variations in the O/Zn concentration ratio of the ZnO films measured by AES. The films were

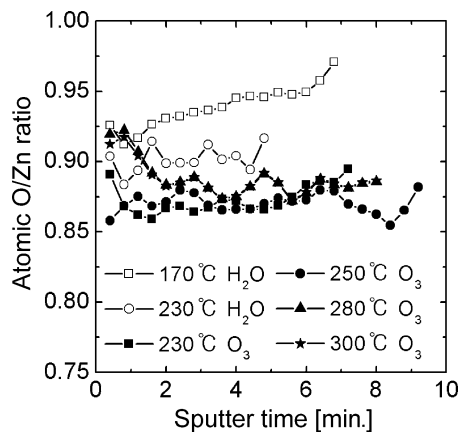


Fig. 5. The variations in the O/Zn concentration ratio of the ZnO films grown using O_3 and H_2O oxidants at various temperatures.

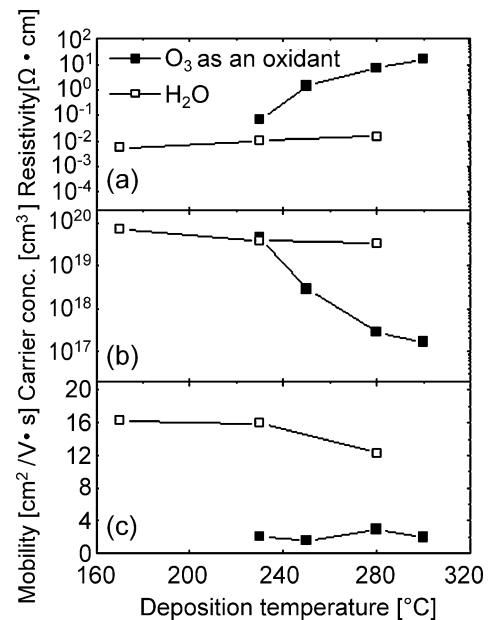


Fig. 6. (a) Resistivity, (b) carrier concentration and (c) mobility of ZnO thin films as a function of the deposition temperature using O_3 and H_2O oxidants, respectively.

grown by using O_3 and H_2O as oxidants, respectively, at various temperatures.

It can be observed that the ZnO films grown with the H_2O oxidant generally have higher O/Zn ratios than those of the films grown with O_3 . This might be due to the residual OH^- ions in the film, due to the insufficient purging of the excess H_2O at such a low T_g ($<200^\circ C$). This can be confirmed by the decreasing O/Zn ratio with increasing T_g because the higher T_g is the more effective in the purging of the excess H_2O . However, the ZnO films grown with the O_3 oxidant show a slightly increasing O/Zn ratio with an increasing T_g due to the higher oxidation of the DEZ molecules at a higher T_g .

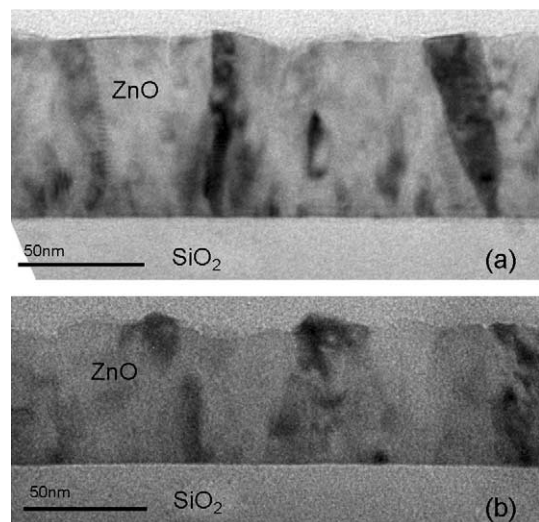


Fig. 7. The cross-section TEM micrographs of the ZnO films grown with (a) O_3 and (b) H_2O at $230^\circ C$.

ZnO is a nonstoichiometric compound with a nominal formula of $\text{Zn}_{1+\delta}\text{O}$, where the excess Zn^{2+} ions are positioned at the interstitial sites (Zn_i^{2+}). Free electrons associated with Zn_i^{2+} ions make the material an *n*-type semiconductor. Therefore, increasing the O/Zn ratio of the films grown with the O_3 oxidant with the increasing T_g results in a decreasing carrier concentration and increasing resistivity as long as $\text{O/Zn} < 1$.

Fig. 6(a)–(c) shows the variations in the resistivity, the carrier concentration (electron) and the carrier mobility as a function of T_g for the cases of the ZnO films grown with O_3 or H_2O as oxidant, respectively. In general, the resistivity of the films grown with O_3 is 10–1000 times larger than that of the films grown with H_2O because of the smaller carrier concentration and mobility, as shown in Fig. 6(b) and (c). The decrease in the carrier concentration with increasing T_g for the O_3 -oxidant-grown films (Fig. 6(b)) is due to the increasing O/Zn ratio, as shown in Fig. 5. It should be noted that the change in the O/Zn ratio with the change in T_g from 230 to 300 °C is only ~2% (Fig. 5), but the decrease in the carrier concentration is approximately three orders of magnitude. This is because the change in the defect (Zn_i^{2+}) density from 10^{20} to 10^{17} cm^{-3} corresponds to <1% change in the relative O/Zn ratio.

It is strange that the resistivity of the films grown with the O_3 oxidant is larger than that of the films grown with the H_2O oxidant despite the O/Zn ratio of the films grown with O_3 being lower than that with the H_2O oxidant. Therefore, the reasons for the high resistivity of the films grown with the O_3 oxidant were investigated.

The carrier mobility can be influenced by the film microstructure, particularly the grain shapes and sizes, for the cases of polycrystalline films, such as ZnO films. Fig. 7(a) and (b) shows the cross-section TEM micrographs of the ZnO films grown with the O_3 and H_2O oxidant, respectively, at a T_g of 230 °C. It can be observed that both films are composed of columnar grains with approximately the same grain sizes (~40 nm in diameter). AFM shows that the film surface roughness is also similar. So, the difference of carrier mobility in these ZnO films is not due to the film microstructure.

Fig. 8 shows the SIMS depth profile results of the ZnO films grown using (a) O_3 and (b) H_2O as oxidant at a T_g of 230 °C. The oxygen profiles are similarly constant throughout the thickness for both samples. However, the ZnO film grown using the O_3 oxidant has a higher Si impurity concentration and a slightly lower Zn concentration, especially near the film/substrate interface compared to the film grown with H_2O . The ZnO film grown using H_2O shows an almost negligible Si impurity concentration and thus shows a constant Zn profile throughout the thickness. Si diffusion into ZnO films for the case of the O_3 oxidant may be due to the strong oxidation power of O_3 . It is believed that the carriers are mostly scattered by defects, not by phonons, at room temperature in ZnO. The higher Si impurity concentration in O_3 -ZnO films mostly

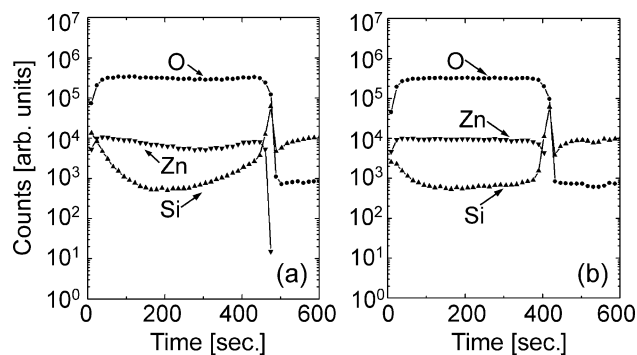


Fig. 8. SIMS composition profiles of ZnO films grown with (a) O_3 and (b) H_2O at 230 °C.

scatters the carriers, so the carrier mobility must be lower than that of the films grown with the H_2O oxidant. It can be observed that the increase in the resistivity of the O_3 -ZnO films compared to that of the H_2O -ZnO almost coincide with the decrease in the mobility (Fig. 6(a),(c)) when the films were grown at a T_g of 230 °C.

4. Conclusions

ZnO films were successfully deposited by ALD using DEZ and O_3 at growth temperatures ranging from 230 to 300 °C. Self-limiting growth was also achieved. The films had a good uniformity in thickness due to the self-limiting mechanism of atomic layer deposition.

ZnO film using O_3 as oxidant revealed a *c*-axis-preferred orientation at the growth temperature ranging from 230 to 300 °C. The resistivity of the ZnO thin films using O_3 as oxidant is 10–1000 times higher than that of films using H_2O as oxidant. The higher resistivity of ZnO thin films with O_3 may be caused by the Si diffusion into the ZnO films and *c*-axis-preferred crystalline orientation.

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References

- [1] H. Nanto, T. Minami, S. Takata, J. Appl. Phys. 60 (1986) 482.
- [2] J.Q. Xu, Q.Y. Pan, T.A. Shun, Z.Z. Tian, Sens. Actuators, B, Chem. 66 (2000) 277.
- [3] S. Muthukumar, N.W. Emanetoglu, G. Patounakis, C.R. Gorla, S. Liang, Y. Lu, J. Vac. Sci. Technol., A 19 (2001) 1850.
- [4] T. Minami, H. Kumagai, T. Kakumu, S. Takata, M. Ishii, J. Vac. Sci. Technol., A 15 (1997) 1069.

- [5] H. Sato, T. Minami, S. Takata, T. Mouri, N. Ogawa, *Thin Solid Films* 220 (1992) 327.
- [6] R.F. Service, *Science* 276 (1997) 895.
- [7] T. Minami, T. Miyata, T. Yamamoto, H. Toda, *J. Vac. Sci. Technol., A* 18 (2000) 1584.
- [8] Y. Kashiwaba, K. Sugawara, K. Haga, H. Watanabe, B.P. Zhang, Y. Segawa, *Thin Solid Films* 411 (2002) 87.
- [9] E.B. Yousfi, J. Fouashe, D. Lincot, *Appl. Surf. Sci.* 153 (2000) 223.
- [10] V. Lujala, J. Skarp, M. Tammenmaa, T. Suntola, *Appl. Surf. Sci.* 82/83 (1994) 34.
- [11] C.H. Liu, R.P.H. Chang, *J. Chem. Phys.* 116 (2002) 8139.
- [12] M. Ylilammi, *Thin Solid Films* 279 (1996) 124.