Ultrathin silicon oxide film on Si(100) fabricated by highly concentrated ozone at atmospheric pressure ⊘

K. Nakamura; S. Ichimura; A. Kurokawa; K. Koike; G. Inoue; T. Fukuda

Check for updates

View Online   Export Citation

Articles You May Be Interested In

Preoxidation treatments for very thin oxides grown after silicon exposure to reactive ion etching plasma

J. Vac. Sci. Technol. B (January 1988)

Suppression of orange-peel coupling in magnetic tunnel junctions by preoxidation

Appl. Phys. Lett. (April 2006)

Process window extension of TiN diffusion barrier using preoxidation of Ru and RuO x film for (Ba,Sr)TiO 3 dielectric film

J. Vac. Sci. Technol. A (July 2001)

14 March 2025 14:15:49

Ultrathin silicon oxide film on Si(100) fabricated by highly concentrated ozone at atmospheric pressure

K. Nakamura,[a] S. Ichimura, and A. Kurokawa
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan

K. Koike, G. Inoue, and T. Fukuda
Shiga Technology Center, Iwatani International Corporation, 4-5-1 Katsube, Moriyama, Shiga 524-0041, Japan

We have investigated ultrathin silicon oxide film growth by highly concentrated ozone at atmospheric pressure. Oxide film >2 nm was grown on as-received Si(100) even at room temperature. The etching rate by dilute hydrofluoric acid solution of oxide fabricated on Si(100) at $350\,°C$ by this method was almost the same as that of thermally grown oxide so that film density is equivalent to that of thermally grown oxide. The etching rate of this film also shows no dependence on the film depth. This is indicating that the transition layer due to the lattice mismatch of substrate and oxide is limited within a thinner region than that of thermally grown oxide. It also indicates that an oxide film with higher film density can be synthesized on the surface with preoxide film already formed to protect bare substrate surfaces. © *1999 American Vacuum Society.*
[S0734-2101(99)17204-X]

I. INTRODUCTION

Use of oxidant gas more reactive than a conventional one such as molecular oxygen or water vapor is expected to implement silicon oxidation at lower substrate temperature which is required for scaling down the size of microelectronics devices in the near future. Ozone[1] is one such alternative which has been shown to enhance the oxidation rate at comparably lower substrate temperature.[2–6] Although these studies have been performed with a conventional ozonizer with an ozone concentration $<10\%$, increasing the concentration of ozone has the possibility to both enhance the oxidation rate and upgrade the quality of synthesized oxide films.

The development of an ozone jet generator system[7,8] with gaseous ozone of $>80\%$ concentration has so far enabled us to analyze ozone adsorption[9–12] as well as initial oxide growth by ozone[13,14] on silicon surfaces. Such characteristics of ozone have been found to enhance the adsorption rate compared to that of oxygen,[9,10] its kinetics and mechanism affected by preadsorbed species,[11] and formation of thermally stable adsorbed species at higher substrate temperature.[12] Initial oxide film >1 nm was successfully grown on Si(100)2×1 by exposing it to ozone at $700\,°C$ for 90 min.[13] However, decreasing substrate temperature to $<500\,°C$ lowered the oxidation rate so that only ultrathin oxide layers <1 nm were fabricated.[14] All the experiments above with the ozone jet generator system have been performed in an ultrahigh vacuum (UHV) environment: ozone pressure at 8×10^{-4} Pa at maximum. Therefore, exposure of silicon substrates to ozone at higher pressure with high ozone concentration is required to increase the oxidation rate to synthesize an oxide film >1 nm at lower substrate temperature $<500\,°C$.

This article reports on the fabrication of ultrathin silicon oxide films by ozone at atmospheric pressure. Ultrathin silicon oxide (SiO$_2$) films were fabricated on Si(100) at room temperature (RT) as well as at $350\,°C$ and their thickness reached 2 nm or more, which was confirmed by analysis of Si $2p$ peaks with x-ray photoelectron spectroscopy (XPS). In order to optimize processing conditions, the quality of synthesized films was evaluated by comparing etching rates of fabricated oxide films with dilute hydrofluoric acid (HF) solution because it is known to be sensitive to oxide film density.[15]

II. EXPERIMENT

The preparation of highly concentrated ozone at atmospheric pressure for the formation of SiO$_2$ thin films on silicon substrates is presented here briefly as follows. The details will be described elsewhere.[16] First, a conventional electric discharge-type ozonizer produced ~5 vol % ozone from oxygen, a source gas. Next, this mixture of ozone and oxygen was introduced into an ozone adsorption column. Here mainly ozone in a mixture of ozone and oxygen gas was adsorbed on silca gel at a low temperature (<210 K) and most of the oxygen gas was evacuated. Then the temperature of silica gel was increased up to room temperature so that the adsorbed ozone/oxygen mixture gas with ozone concentration $>70\%$ was desorbed from the silica gel. For exposure of silicon substrates, we employed two different conditions: filled-up condition and continuous flowing condition. For the filled-up condition, this gas was directly introduced into and stored in a processing chamber which was already evacuated. For the continuous flowing condition, ozone gas desorbed from silica gel was first introduced and stored in an ozone storage vessel. Then, ozone vapor in this storage vessel was introduced into the processing chamber at a constant flowing rate. Specimens in this chamber were ex-

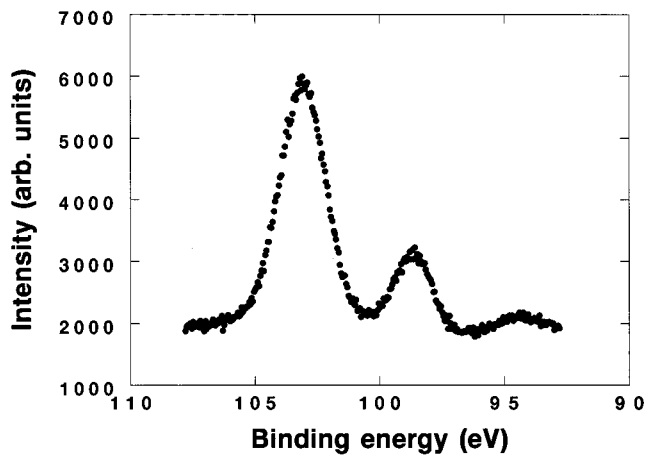[a]Author to whom correspondence should be addressed; electronic mail: ken@etl.go.jp

FIG. 1. XPS Si $2p$ spectra of thermally grown oxide on Si(100). Oxide thickness measured by ellipsometry is 4.2 nm.

FIG. 2. XPS Si $2p$ spectra of oxide fabricated on Si(100) at RT by atmospheric pressure ozone (740 Torr) for 54 h.

posed to ozone reaching atmospheric pressure either under filled-up condition or under flowing condition.

This ozone gas at atmospheric pressure was supplied directly to as-received Si(100) wafer with 0.8 nm native oxide which was already set in the processing chamber. Three other oxides were also prepared for comparison: (i) thermally grown oxide, (ii) ozone oxide fabricated at reduced pressure in UHV at 700 °C, and (iii) native oxide. Thermal oxide was grown in a wet atmosphere with water vapor in a furnace while the substrate temperature was kept at 750 °C. Oxide film by ozone at 8×10^{-4} Pa was synthesized in UHV by another ozone jet generator system[7,8] following the preparation of clean and reconstructed Si(100)2×1 by heating the Si(100) sample up to 1200 °C and subsequently cooling down. Native oxide was formed in the air on hydrogen-terminated Si(100) at RT.

Film thickness of prepared oxides was estimated by measuring the ratio of two Si XPS $2p$ peaks from silicon substrate and silicon oxide between 99 and 103 eV.[17,18] Photoelectrons excited by Mg $K\alpha$ x rays were analyzed by a double-pass cylindrical mirror analyzer in an analysis chamber. The analyzer was operated with a pass energy of 50 eV for each scan. The take-off angle was 42° to the surface normal.

The etching rate of oxide film by dilute HF solution was evaluated by plotting oxide film thickness estimated by use of Si $2p$ XPS peaks versus etching time. After each oxidation process, the following procedures were repeated for each etching period. First, the sample with synthesized oxide was moved out of the processing chamber. It was next dipped into and stirred in a 0.1 wt % HF solution at 25 °C. Then it was removed and stirred in pure water for 2 min for rinsing. Finally it was taken out of the water, blown by air to remove water on the sample surface, and introduced into the UHV chamber for XPS analysis.

III. RESULTS

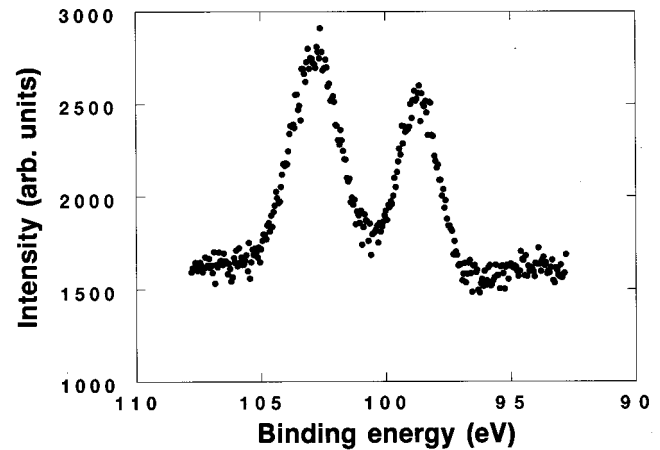Figure 1 indicates XPS Si $2p$ spectra of thermally grown oxide fabricated on Si(100) at 750 °C in a wet environment.

The peak at lower binding energy is attributed to silicon substrate while the peak at higher binding energy is attributed to silicon oxide, i.e., Si^{4+}.[17] Oxide thickness can be also determined by the peak intensity of SiO_2, I_{oxide}, and the peak intensity of substrate, I_{sub}, according to the following relation:[17,18]

$$x = \lambda \cos \theta \ln[1 + (I_{oxide}/I_{sub})(I_{SiO_2}/I_{Si})], \quad (1)$$

where x is oxide thickness, λ is a Si $2p$ photoelectron escape mean free path, θ is a take-off angle, I_{SiO_2} and I_{Si} are Si $2p$ XPS peak intensities of bulk SiO_2 and bulk silicon, respectively. By ellipsometric measurement with the refractive index of 1.462, the thickness of this oxide film was estimated to be 4.2 nm. From the peak ratio I_{oxide}/I_{sub} of oxide at 4.2 nm in Fig. 1 with $\theta = 42°$, Eq. (1) can be described as follows:

$$x = 2.0 \ln[1 + 1.8(I_{oxide}/I_{sub})](nm). \quad (2)$$

Here we employed $\lambda = 2.7$ nm which was theoretically obtained[19] and is in good agreement with an experimentally obtained value.[20] Equation (2) was used to determine oxide thickness in the following measurement.

Ozone gas at atmospheric pressure was exposed to as-received Si(100) at RT. Figure 2 indicates XPS Si $2p$ spectra of the SiO_2 thin film fabricated on as-received Si(100) by ozone at atmospheric pressure (9.9×10^4 Pa or 740 Torr) for 54 h. The sample was set in the processing chamber followed by ozone introduction to fill the chamber. Thickness of the synthesized oxide film was evaluated to be 2.6 nm, where the thickness of native oxide on as-received wafer was 0.8 nm. To increase this thickness at RT, the sample was exposed for another 168 h. During this oxidation time, we evacuated and refilled the ozone gas twice in the chamber to avoid exposing the sample to dissociated species of ozone. However, no apparent increase was observed by longer oxidation time at RT. Film growth appeared to be saturated at the thickness ~3 nm under this condition in the processing chamber full of ozone at atmospheric pressure.
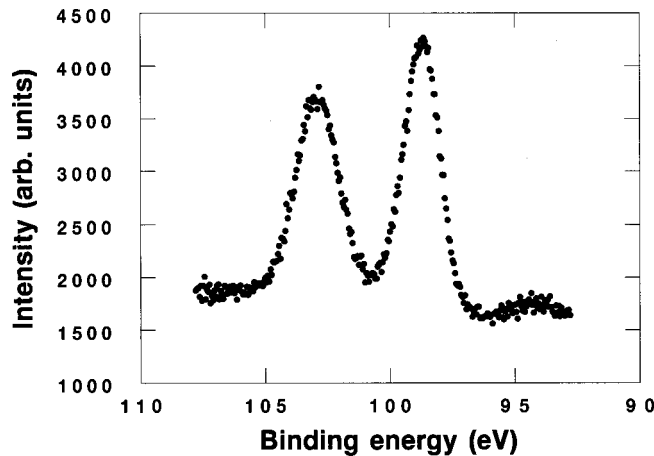
FIG. 3. XPS Si 2*p* spectra of oxide fabricated on Si(100) at 350 °C by atmospheric pressure ozone (740 Torr) flowing at 200 sccm for 25 min.

FIG. 5. XPS Si 2*p* spectra of native oxide fabricated on Si(100) in air for 90 h after HF treatment.

Ozone gas at atmospheric pressure was also exposed to as-received Si(100) while flowing ozone gas through the processing chamber at 200 sccm and keeping the same pressure $(9.9 \times 10^4$ Pa or 740 Torr) inside the chamber. However, under this flowing condition, increase of oxide film thickness in addition to original native oxide was not clearly observed on surfaces either at RT or 100 °C during the oxidation time < 1 h. So we raised the substrate temperature to enhance the oxidation rate. Figure 3 indicates XPS Si 2*p* spectra of the ultrathin oxide film fabricated on as-received Si(100) at 350 °C for 25 min. Ultrathin oxide film with its thickness estimated to be 1.9 nm was grown on the surface during this processing time.

These oxides have been etched by dilute HF solution. Figure 4 indicates change of oxide thickness evaluated by the ratio of XPS Si 2*p* peaks during the etching by 0.1 wt % HF solution at 25 °C. Etched oxides are (◆) thermally grown oxide, (□) oxide fabricated by ozone at atmospheric pres-

sure at RT, (○) oxide fabricated by ozone at atmospheric pressure at 350 °C, and (■) oxide fabricated by ozone at 8×10^{-4} Pa at 700 °C. Ozone oxide with thickness of 1.9 nm fabricated at 350 °C has the same etching rate as that of thermally grown oxide or that of ozone oxide at 700 °C in UHV: 1.2 Å/min. Ozone oxide at RT has the faster etching rate: 33 Å/min. On each of these ozone oxide films, its etching rate is constant in the whole thickness. The etching rate of thermally grown oxide is also 1.2 Å/min in the outermost layers. Close to the interface region below the thickness of about 1.2 nm, its etching rate becomes slower. However, such change in etching rates was not observed for the other three kinds of ozone oxide films. The etching rate of native oxide on as-received surface, not plotted in Fig. 4, was estimated to be 3.0 Å/min.

Figure 5 indicates XPS Si 2*p* spectra of Si(100) with native oxide formed intentionally in the air. This sample was exposed to the atmospheric air in 90 h at 25 °C with atmospheric humidity of 35% after dipping the sample into 1% HF solution to remove original native oxide and to terminate dangling bonds by hydrogen atoms. The atmosphere air containing oxygen and moisture could form a native oxide thin film only up to 6 Å. Further exposure indicated no increase in the thickness so that it has reached the saturated thickness under this condition of pressure and temperature.

IV. DISCUSSION

Ozone exposure at atmospheric pressure can oxidize silicon substrate to form oxide ~ 2 nm at lower temperature. The previous report[13] indicates that oxide growth at 700 °C by ozone under UHV condition reached oxide thickness of more than 1 nm, while growth by molecular oxygen reached saturation of less than 1 nm. However, at temperatures below 500 °C, it was difficult to obtain oxide film with thickness > 1 nm at reduced pressure in 90 min even by ozone in an UHV environment.[14] These results suggest the different kinetics of oxide growth rate, also by ozone, with a different film thickness. Hence, to increase the rate of oxide growth
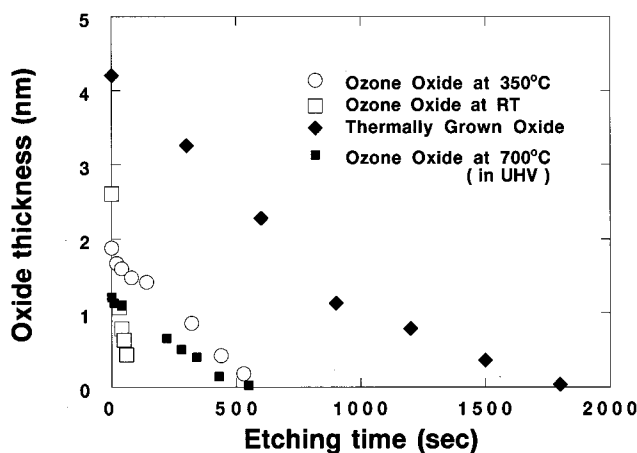

FIG. 4. Oxide thickness on Si(100) during etching process by 0.1 wt% HF solution at 25 °C. Samples are (◆) thermally grown oxide, (○) oxide fabricated on Si(100) at 350 °C by atmospheric pressure ozone, (□) oxide fabricated on Si(100) at RT by atmospheric pressure ozone, and (■) oxide fabricated on Si(100)2×1 at 700 °C by 8×10^{-4} Pa ozone.
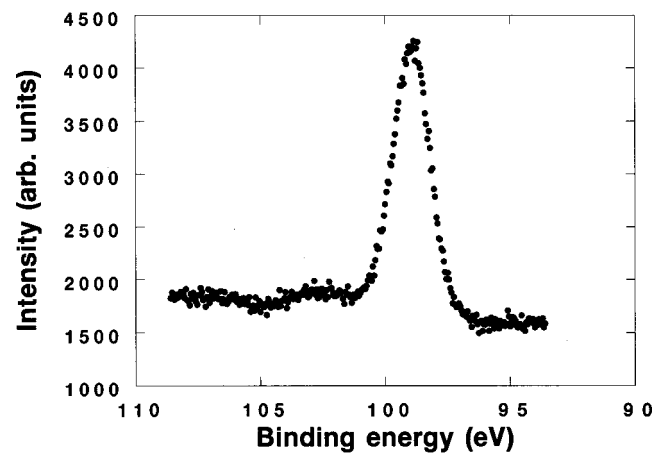
while keeping substrate temperature as low as possible, it was necessary to increase ozone pressure. Ozone exposure at atmospheric pressure is proven to be so effective as to complement lower kinetics of oxide growth above a few oxide layers under an appropriate condition. This reactivity of ozone is also clear if we compare oxide growth by atmospheric air including oxygen and moisture water only reaching the thickness of 0.6 nm even after exposing the sample to the air for 90 h in Fig. 5.

Although the oxidation rate or thickness of the synthesized film by ozone at atmospheric pressure is satisfactory at RT, the substrate temperature must be optimized to maintain or improve quality of the film as good as that of thermally grown oxide. In the case of setting the sample at RT inside the chamber filled with ozone, oxide film >2 nm was grown on as-received Si substrate. However, its etching rate is so rapid as to be 33 Å/min, much faster than 1.2 Å/min of thermally grown oxide. The etching rate of oxide by HF solution is sensitive to oxide film density, porosity, and composition.[15] One possible reason for this fast etching rate is, therefore, the formation of porosity by ozone irradiation to enhance further oxidation rate[21] which is irrelevant for device use. Under the flowing condition of ozone at atmospheric pressure, oxide growth is negligibly small at RT, but this means that negative damage on the substrate is also avoidable. We think that, between the two mentioned above, flowing condition is a better selection for oxide fabrication with the substrate temperature as low as possible: for example at 350 °C as is discussed below.

The oxide film fabricated on Si(100) at 350 °C by flowing ozone at atmospheric pressures is expected to have film density as high as that of thermally grown oxide while its thickness reached about 2 nm, because the initial etching rate of thermally grown oxide and that of ozone oxide at 350 °C are almost identical at 1.2 Å/min. This is consistent with our recent observation that oxide films at lower substrate temperature made by ozone at 8×10^{-4} Pa are also expected to be as dense as thermally grown oxide, although, in this case, thickness could not reach more than 1 nm.[14] Therefore, by use of ozone at atmospheric pressure, not only film quality but also thickness or oxidation rate has been improved.

An additional feature of ozone oxide is that its etching rate by HF solution is constant and independent of film depth while thermally grown oxide shows its dependence. Due to the lattice mismatch of structures of Si and SiO_2, there exists a region called the transition layer between substrate and oxide to relax stress to avoid strain in the interface.[17,22,23] It is reported that, due to the existence of such transition layer, the etching rate of ultrathin silicon oxide is not constant during the whole etching time,[24,25] which is also observed in the measurement of our sample of thermally grown oxide at the thickness around 1.2 nm. However, such change in the etching rate is not observed, for example, in the case of ozone oxide at 350 °C in Fig. 4. Therefore, the transition layer between Si and SiO_2 in this oxide at 350 °C is expected to be thinner than that of thermally grown oxide, which is a relevant characteristic for the use in microelectronics devices.

The constant etching rate of ozone oxide at 350 °C also shows the possibility to synthesize an oxide film with higher film density after a preoxide film was formed to protect bare substrate surfaces. As was noted, ozone oxide was fabricated on as-received Si(100) surface at 350 °C with its native oxide of 0.8 nm. The etching rate of native oxide is evaluated to be 3.0 Å/min which is faster than ozone oxide at 350 °C. However, the etching rate of ozone oxide at 350 °C is constant at 1.2 Å/min during the whole etching time without any change around the thickness of 0.8 nm. This means that the property of the whole film, i.e., oxide film density, has become homogeneous, even though the oxide was synthesized on the substrate with originally existing native oxide.

Therefore, in the case of ozone, it is expected that incident ozone molecules or oxygen atoms released from ozone molecules not only adsorb on the outermost layer but also diffuse into or at least have an affect on already existing oxide layers on surfaces at lower substrate temperature. Oxide growth by molecular oxygen on silicon surfaces in the region of ultrathin layers is considered to initiate with a layer-by-layer oxidation mechanism.[26–29] However, oxidation by ozone of as-received Si(100) with native oxide is expected to proceed with not only this layer-by-layer mechanism but also with another mechanism of oxygen reaction with incompletely oxidized silicon in the transition layer which has been reported in the case of thermal oxidation.[30] This mechanism is expected to upgrade the density of native oxide equivalent to that of thermally grown oxide.

Whether on clean Si(100)2×1 (Ref. 14) or on upgraded as-received Si(100), stepwise decrease of oxidation rate by ozone is suggesting a layer-by-layer oxide growth mechanism. We often observed that the oxide stops growing or appears to stop growing at some thickness under an ozone exposure condition but that it starts growing by increasing substrate temperature or gas pressure. This indicates that growth kinetics are very sensitive to the thickness of fabricated oxide layers. Such decrease of oxidation rate during the film growth is, we think, due to the layer-by-layer growth mechanism of ozone oxide films. In the case of Si(100) with native oxide, we believe that oxidation by ozone starts with a reaction of ozone with native oxide prior to the layer-by-layer ozone oxide growth. Kinetics and mechanism of oxide synthesis by ozone, therefore, must be analyzed and described, respectively, on clean Si(100)2×1, on Si(100) with native oxide, and on ozone oxide films under the filled-up condition and the flowing condition of ozone gas. A detailed study which is underway will clarify each oxidation mechanism.

V. CONCLUSION

Synthesis of ultrathin oxide films by ozone at atmospheric pressure was investigated. Oxide film >2 nm was grown on as-received Si(100) even at RT while the sample was set in the chamber full of ozone at atmospheric pressure. This was not implemented on Si(100)2×1 by exposing it to ozone at reduced pressures in UHV for 90 min. To improve film quality, another oxide film was grown on Si(100) at 350 °C by

flowing ozone gas at 200 sccm. This oxide film ~2 nm has almost the same film density as that of thermally grown oxide shown by comparing etching rates by HF solution. It is also indicated that the transition layer of this film is limited within a thinner region than that of thermally grown oxide. The constant etching rate during the whole etching time shows the possibility of synthesizing an oxide film with higher film density after a preoxide film was formed to protect bare substrate surfaces.

[1] M. Horváth, L. Bilitzky, and J. Hüttner, *Ozone* (Elsevier, New York, 1985), p. 44.

[2] I. W. Boyd, V. Graciun, and A. Kazor, Jpn. J. Appl. Phys., Part 1 **32**, 6141 (1993).

[3] S. C. Chao, R. Pitchai, and Y. H. Lee, J. Electrochem. Soc. **136**, 2751 (1989).

[4] A. Kazor and I. W. Boyd, Electron. Lett. **29**, 115 (1993).

[5] A. Kazor and I. W. Boyd, Appl. Phys. Lett. **63**, 2517 (1993).

[6] A. Kazor, R. Gwilliam, and I. W. Boyd, Appl. Phys. Lett. **65**, 412 (1994).

[7] S. Hosokawa and S. Ichimura, Rev. Sci. Instrum. **62**, 1614 (1991).

[8] S. Ichimura, S. Hosokawa, H. Nonaka, and K. Arai, J. Vac. Sci. Technol. A **9**, 2369 (1991).

[9] A. Kurokawa and S. Ichimura, Jpn. J. Appl. Phys., Part 2 **34**, L1606 (1995).

[10] K. Nakamura, A. Kurokawa, and S. Ichimura, J. Vac. Sci. Technol. A **15**, 2441 (1997).

[11] K. Nakamura, A. Kurokawa, and S. Ichimura, Surf. Sci. **402–404**, 165 (1998).

[12] K. Nakamura, A. Kurokawa, and S. Ichimura, Surf. Interface Anal. **25**, 88 (1997).

[13] A. Kurokawa, S. Ichimura, and D. W. Moon, Mater. Res. Soc. Symp. Proc. **477**, 359 (1997).

[14] K. Nakamura, A. Kurokawa, and S. Ichimura, Thin Solid Films (in press).

[15] For example, W. A. Pliskin, J. Vac. Sci. Technol. **14**, 1064 (1977).

[16] K. Koike, G. Inoue, T. Fukuda, S. Ichimura, A. Kurokawa, and K. Nakamura, Rev. Sci. Instrum. (to be published).

[17] F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, Phys. Rev. B **38**, 6084 (1988).

[18] D. F. Mitchell, K. B. Clark, J. A. Bardwell, W. N. Lennard, G. R. Massoumi, and I. V. Mitchell, Surf. Interface Anal. **21**, 44 (1994).

[19] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. **17**, 927 (1991).

[20] Z. H. Lu, J. P. McCaffrey, B. Brar, G. D. Wilk, R. M. Wallace, L. C. Feldman, and S. P. Tay, Appl. Phys. Lett. **71**, 2764 (1997).

[21] W. H. Thompson, Z. Yamani, L. H. Abu Hassan, J. E. Greene, M. Nayfeh, and M.-A. Hasan, J. Appl. Phys. **80**, 5415 (1996).

[22] F. J. Grunthaner, P. J. Grunthaner, R. P. Vasquez, B. F. Lewis, J. Maserjian, and A. Madhukar, Phys. Rev. Lett. **43**, 1683 (1979).

[23] Q. Liu, J. F. Wall, and E. A. Irene, J. Vac. Sci. Technol. A **12**, 2625 (1994).

[24] T. Suzuki, M. Muto, M. Hara, K. Yamabe, and T. Hattori, Jpn. J. Appl. Phys., Part 1 **25**, 544 (1986).

[25] H. Yamagishi, N. Koike, K. Imai, K. Yamabe, and T. Hattori, Jpn. J. Appl. Phys., Part 2 **27**, L1398 (1988).

[26] M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, and M. Ohwada, J. Appl. Phys. **68**, 1272 (1990).

[27] M. Morita and T. Ohmi, Jpn. J. Appl. Phys., Part 1 **33**, 370 (1994).

[28] J. R. Engstrom, D. J. Bonner, and T. Engel, Surf. Sci. **268**, 238 (1992).

[29] H. Watanabe, K. Kato, T. Uda, K. Fujita, M. Ichikawa, T. Kawamura, and K. Terakura, Phys. Rev. Lett. **80**, 345 (1998).

[30] E. P. Gusev, H. C. Lu, T. Gustafsson, and E. Garfunkel, Phys. Rev. B **52**, 1759 (1995).