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Effect of Ion Bombardment on the Chemical and the Mechanical Properties of Silicon-Nitride Thin Films Deposited by Using PECVD with $SiH_4/NH_3/Ar$ Gases at Low Temperature

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The influence of the ion bombardment energy controlled by using the d.c. bias voltage from no-bias to –200 V on the chemical and the mechanical properties of Si_xN_y deposited by plasma enhanced chemical vapor deposition (PECVD) at substrate temperatures lower than 100 °C was investigated for applications to thin film diffusion barriers for organic electronic devices. The deposited film was a silicon-rich Si_xN_y thin film having oxygen and hydrogen as major impurities. A change in the d.c. bias voltage up to –200 V during the deposition changed the properties, such as the stress, the hardness, the surface roughness, *etc.* in addition to the deposition rate. A lower stress, a harder material, and a smoother surface could be obtained by applying a moderate bias voltage of about –100 V through a change in the bonding states of the oxygen impurity in the film, a densification of the film, and an increased surface mobility of the deposited atoms.

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I. INTRODUCTION

Silicon nitride (Si_xN_y) is a material that has been used in various applications, such as passivation layers for diverse microelectronics, a gate dielectric material for thin film transistors including organic thin film transistors (OTFTs), *etc.*, due to their chemical inertness, excellent dielectric properties, and thermal stability [1–5]. Generally, Si_xN_y is deposited by using chemical vapor deposition (CVD) or plasma enhanced CVD (PECVD) at temperatures higher than a few hundred degrees. The deposition of Si_xN_y at a high temperature not only improves the mechanical and the chemical properties of the thin films but also reduces the stress in the film. However, in some applications such as thinfilm passivation of organic light emitting diodes and OTFTs, depositions on plastic substrates, *etc.*, high-temperature processing is not suitable [6,7]. In fact, the use of PECVD instead of CVD in the deposition of Si_xN_y decreases the deposition temperature by using the plasma to dissociate the gas molecules to be deposited, such as SiH_4 and NH_3, before the gas molecules reach the substrate [8]; therefore, if a high-density plasma, such as an inductively coupled plasma (ICP), is used instead of a capacitively coupled plasma, the deposition temperature can be further decreased even though low-temperature deposition has some disadvantages, such as the enhanced sensitivity to moisture and the environment, *etc.* [9].

The ion bombardment of the substrate during the deposition of Si_xN_y by negatively biasing the substrate can also help in decreasing the deposition temperature and in changing the chemical and the mechanical properties. In this study, Si_xN_y was deposited using an ICP plasma by varying the substrate bias voltage at temperatures lower than 100 °C, and the effect of the biasing voltage on the chemical and the mechanical properties of the Si_xN_y was investigated.

II. EXPERIMENT

A schematic diagram of the PECVD system used in this experiment is shown in Figure 1. The plasma source was an ICP source having a spiral inductive coil made of a 3.5-turn copper located on the top of the processing chamber and separated by a SiO_2 plate to transmit the electromagnetic field from the coil to the chamber. A rf power of 13.56 MHz was applied to the ICP coil through a L-type matching network. The substrate was biased with another 13.56-MHz rf power supply, and the bias voltage was varied from no-bias to –200 V for ion bombardment of the substrate during the processing. At

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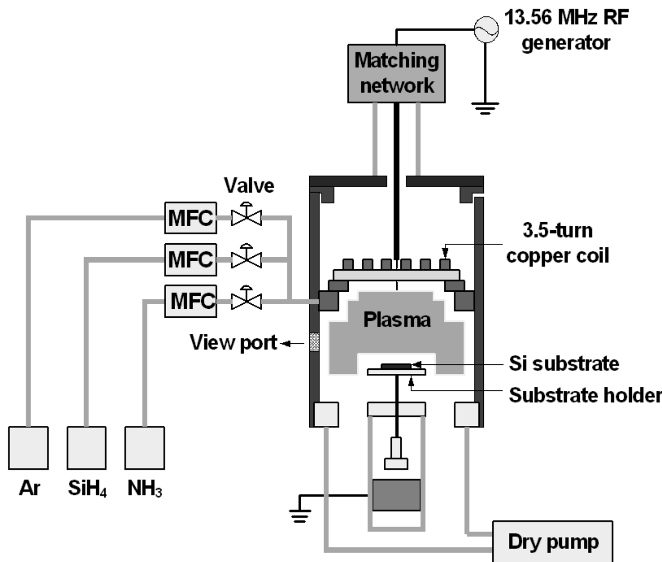

Fig. 1. Schematic diagram of the ICP PECVD system used in the experiment.

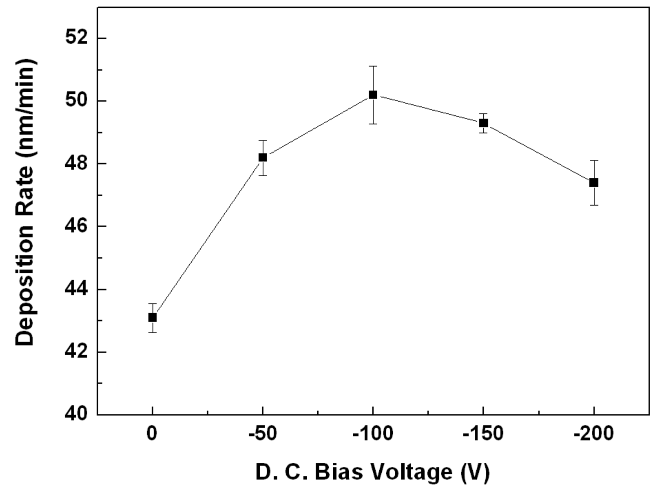

Fig. 2. Deposition rate of Si_xN_y thin films as a function of the d.c. bias voltage from no-bias to –200 V, R = $NH_3/(NH_3 + SiH_4)$ = 0.4, $NH_3 + SiH_4$ = 10 sccm, Ar = 25 sccm, rf power = 200 W and substrate temperature <100 °C.

the no-bias condition, due to the floating potential, a self bias of –20 V was induced.

The sample was a p-type <100> silicon wafer, and Si_xN_y was deposited at a 200 W rf power by using SiH_4 (6 sccm)/NH_3 (4 sccm)/Ar (25 sccm, dilution gas) and biasing the substrate without heating the substrate. Even though the substrate was not heated, the sample was heated by the plasma and by the ion bombardment during the biasing; therefore, the substrate temperature could be kept lower than 100 °C by using a chiller. A dry pump was used to evacuate the chamber, and the working pressure was maintained at 80 mTorr.

The film thickness was measured using an α-step profilometer (Tencor Inc. Alpha-step 500). The compositions and the binding states of Si_xN_y films were measured using X-ray photoelectron spectroscopy (XPS, VG Microtech Inc., ESCA2000). The binding states were also measured by using a fourier transform infrared spectrometer (FT-IR; Bruker, Bruker IFS-66/S) for the wavenumber range of 600 $\sim$ 4000 cm^{-1} with a silicon wafer as a reference sample. The hardness of the thin films was determined by using a nanoindenter (MTS, NanoIndenter XP), and the surface roughness was observed by using an atomic force microscope (AFM, SII Nano Technology. Inc, SPA-300 HV) in the non-contact mode. The stress of the thin films was evaluated by measuring the convex curvature of the substrate before and after the deposition (Frontier Semiconductor, FSM 500 TC) at 25 °C.

III. RESULTS AND DISCUSSION

Figure 2 shows the deposition rate of Si_xN_y measured as a function of the applied d.c. bias voltage at a 200 W rf power by using SiH_4 (6 sccm)/NH_3 (4 sccm)/Ar (25 sccm). As the figure shown, an increase in the applied bias voltage from no-bias to –100 V increased the deposition rate from 43 to 50 nm/min, and a further increase in the bias voltage to –200 V decreased the deposition rate slightly. An increased bias voltage increases the substrate temperature by bombarding the surface with higher energy and increases the reactivity of the surface when the bombardment energy of the ion is not too high [10]. However, if the bombardment energy of the ions is too high, the material deposited on the substrate can be sputtered off. Therefore, the increase in the deposition rate with increasing bias voltage is believed to be from the enhanced compound formation by activating the surface while the slight decrease in the deposition rate at bias voltages higher than –100 V is from the sputtering of the deposited material. In addition, an increase in the bias voltage can increase the density of the material deposited. Liao *et al.* [11] found that siliconnitride films prepared by using PECVD at a low temperature had porous structures. Therefore, the slight decrease in the deposition rate at voltages higher than –100 V appears to be partially related to an increase in the density of the film deposited by the bombardment of ions because the film was deposited at a low temperature (lower than 100 °C).

The atomic concentration of the deposited Si_xN_y thin films was measured by using XPS as a function of the substrates d.c. bias voltage, and the results are shown in Figure 3. For the measurement, 150 nm thick Si_xN_y films were deposited on silicon substrates. As the figure shown, Si, C, O, and N were detected as components of the deposited film, and a variation of the d.c. bias voltage did not change the atomic composition significantly. Among the components, carbon appears to be from air

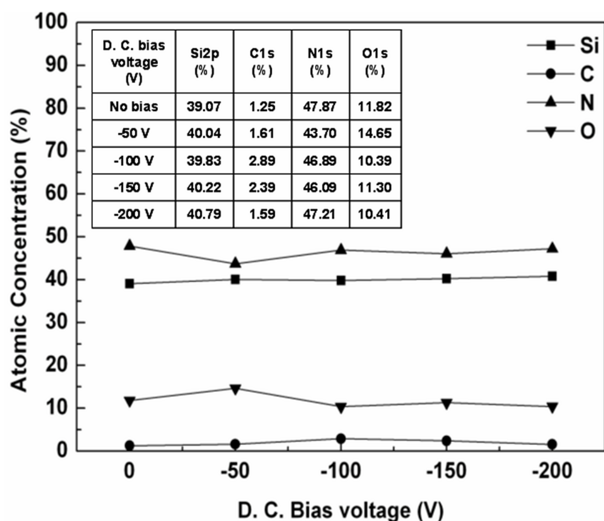

Fig. 3. Atomic concentrations of silicon (Si), nitrogen (N), oxygen (O), and carbon (C) as functions of the d.c. bias voltage. The thickness of all samples is 150 nm. The deposition conditions are the same as those in Figure 2.

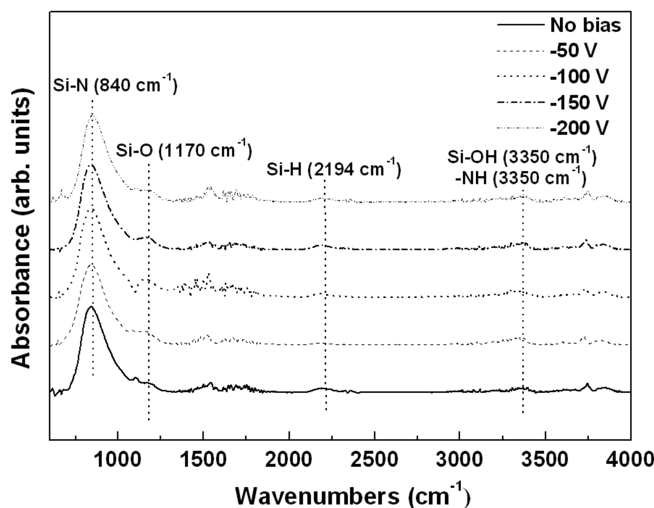

Fig. 5. FT-IR absorption bands related to Si (N, H, O) bondings for various d.c. bias voltages. The deposition conditions are the same as those in Figure 2.

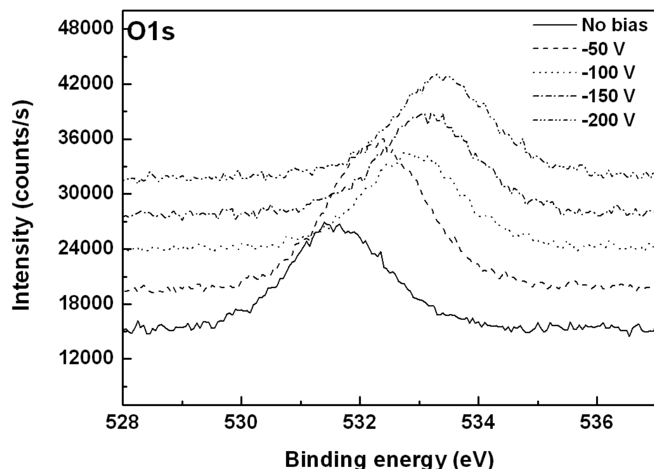

Fig. 4. O1s XPS narrow scan of the oxygen impurity in Si_xN_y thin films as a function of the d.c. bias voltage. The deposition conditions are the same as those in Figure 2.

exposure before the XPS measurement, and oxygen appears to be from the deposition of Si_xN_y at a low vacuum level, thus from impurities, such as oxygen and adsorbed water vapor [12]. The oxygen percentage was relatively high and was in the range from 10 ~ 15 %. Especially, a d.c. bias voltage of about –50 V, the highest oxygen percentage of about 14.7 % was observed, even though the reason for the highest oxygen incorporation is not clear. The ratio of Si:N was in the range from 1.09 to 1.22; therefore, silicon-rich nitride was obtained.

Figure 4 shows the narrow scan XPS data of the O1s peak measured as a function of the d.c. bias voltage for the conditions shown in Figure 3. As the figure shown, the oxygen peak was shifted from about 531.4 to 533.3 eV as the d.c. bias was increased from no-bias to –200 V. The oxygen peaks for Si-O and Si-OH are known to be located at 531.8 and 533.8 eV [13], respectively; therefore, the shift of oxygen with increasing d.c. bias voltage appears to be related to a change in the oxygen binding states from Si-O to Si-OH due to the enhanced incorporation of hydrogen caused by hydrogenion bombardment originating from SiH_4 and NH_3 [14, 15] with increasing d.c. bias voltage [14]. In the case of the Si2p and the N1s peaks, the peaks remain around 102 eV and 397 eV, respectively, which is attributed to Si-N bonding, and no significant variation of the peak shift could be observed due to the high strength of Si-N bonding [not shown].

Hydrogen could not be detected by XPS due to the detection limit even though there was a possibility of hydrogen incorporation in the films. Incorporation of hydrogen in the deposited films could be identified by FTIR. Figure 5 shows the IR absorption spectra measured to estimate the chemical bonding states of 150-nm-thick Si_xN_y thin films deposited as a function of d.c. bias voltage. The IR absorption spectra were recorded in the range of 600 ~ 4000 cm^{-1}. As the figure shown, all the spectra showed a strong absorption band around 840 cm^{-1} that originated from the Si-N bonding [11]. In addition, broadband peaks related to Si-O (1170 cm^{-1}) [16], Si-H (2194 cm^{-1}) [17] and Si-OH (3350 cm^{-1}) [18] or N-H (3350 cm^{-1}) [19] were observed. The Si-O absorption peak is related to the oxygen percentage in the films observed by XPS in Figure 3 even though the highest peak was observed at a d.c. bias voltage of –100 V. However, after –100 V, an increase in the d.c. bias voltage decreased the Si-O bondings. The increase in the Si-OH bonding with increasing d.c. bias voltage could not be easily identified due to the superimposition of the peak related to N-H bonding. Even though the change

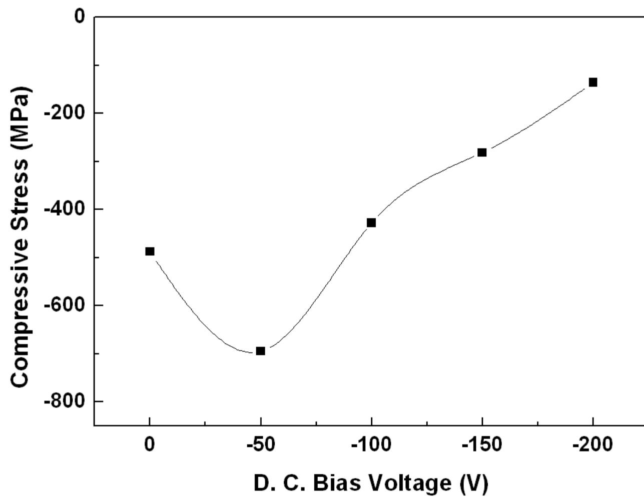

Fig. 6. Stress as a function of the d.c. bias voltage for bias voltage from no-bias to –200 V. The deposition conditions are the same as those in Figure 2.

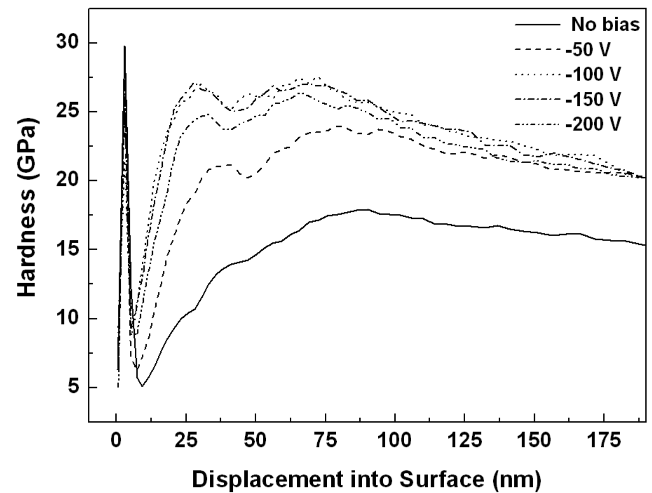

Fig. 7. Hardness of Si_xN_y thin films as a function of the d.c. bias voltage and displacement into surface for bias voltage from no-bias to –200 V. The thickness of all samples is 600 nm. The deposition conditions are the same as those in Figure 2.

in the bonding states with increasing d.c. bias voltage could not be understood clearly, the incorporation of hydrogen in the deposited films could be identified by using the FTIR measurement.

The stress induced on the deposited Si_xN_y thin films was measured. The total stress (σ_t) is obtained from [20]

$$\sigma_t = \frac{E_s . h_s^2}{(1 - v_s) 6Rt} , \quad (1)$$

where $\frac{E_s}{(1-v_s)}$ is the elasticity modulus of the substrate, h_s is the substrate thickness, t is the film's thickness, and R is the effective curvature radius. The measured film stress is shown in Figure 5 as a function of the d.c. bias voltage. As the figure shown, the deposited thin films had compressive stresses for all cases when convex were grown; however, the stress decreased to 136 MPa with increasing bias voltage after the maximum of 694 MPa at a d.c. bias voltage of –50 V. The highest compressive stress shown at a d.c. bias voltage of –50 V appears to be related to the highest oxygen percentage incorporated in the film, as shown in Figure 3 because the Si_xN_y lattice needs to be strained to accommodate the oxygen impurity. The decrease in the stress with further increases in the d.c. bias voltage, however, appears to be related to the change in the oxygen binding states from Si-O to Si-OH, as shown in Figure 4, which releases the stress in a Si_xN_y lattice having an oxygen impurity.

The hardness of the deposited Si_xN_y films was measured as a function of the d.c. bias voltage, and the results are shown in Figure 7. Li *et al.* [21] showed that, when the contact depth exceeded 10 $\sim$ 20 % of the film's thickness, a substrate effect on the contact, the stiffness, the elastic modulus, and the hardness could be observed. Therefore, in this experiment, a 600-nm-thick film was used to measure the hardness to eliminate the effect of the silicon substrate on the measured hardness. At a contact depth of 80 nm, the measured hardness values were 17.6, 23.9, 26.3, 26.5 and 25.2 GPa for dc bias voltages of no-bias, –50, –100, –150 and –200 V, respectively. Therefore, the hardness of the thin films increased with increasing d.c. bias voltages up to –150 V and decreased slightly for a further increase in the d.c. bias voltage to –200 V. The increase in the hardness with increasing d.c. bias voltage up to –150 V is believed to be related to an increased density of the film caused by increasing the bombardment energy. However, when the bombardment energy is too high, then, due to physical damage to the film, the density can be decreased, and the hardness of the film can be decreased. Therefore, the slight decrease in the hardness seen at –200 V appears to be related to damage to the film by ion bombardment.

The surface roughness of the deposited Si_xN_y thin films was measured as a function of the d.c. bias voltage, and the results are shown in Figures 8(a)$\sim$(c) for the AFM images of Si_xN_y thin films on silicon wafers at (a) no-bias, (b) –50 V and (c) –200 V and in Figure 8(d) for the rms values of the surface roughness as a function of the d.c. bias voltage. As the AFM images shown an increase in the d.c. bias voltage decreased the surface roughness uniformly over the sample surface [12]. When the rms roughness were measured, as shown in Figure 8(d), it decreased from 1.108 to 0.1076 nm when the d.c. bias voltage was increased from no-bias to –200 V. Especially, the rms roughness was drastically decreased when the d.c. bias voltage was increased to –100 V and decreased slightly with further increases in the d.c. bias voltage. The decrease in the surface roughness with increasing d.c. bias voltage is related to the increased surface mobility of the atoms deposite by energetic ion

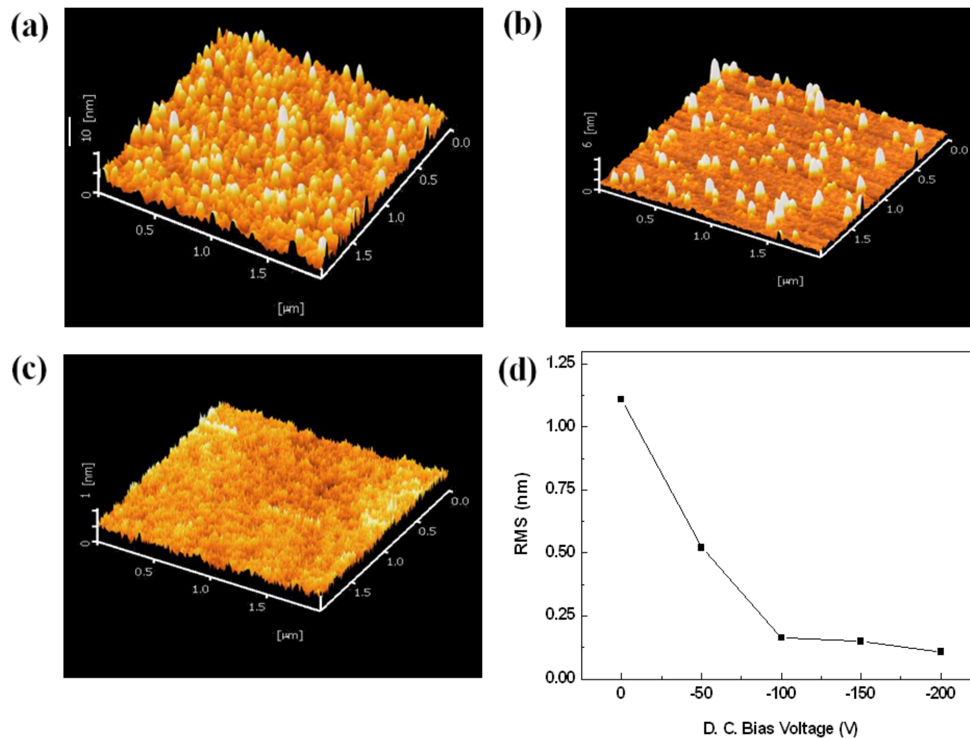

Fig. 8. Morphology and roughness of Si_xN_y thin films as a function of the d.c. bias voltage for bias voltage. The thickness of all samples is 100 nm. The deposition conditions are the same as those in Figure 2. (d) rms roughness of Si_xN_y thin films as a function of the d.c. bias voltage of (a) no bias, (b) –50 V and (c) –200 V.

bombardment [20].

IV. CONCLUSIONS

The effect of ion bombardment during low temperature PECVD on the chemical and the mechanical properties of Si_xN_y thin film was investigated by varying the d.c. bias voltage during the growth of Si_xN_y thin films at temperatures less than 100 °C with SiH_4 (6 sccm)/NH_3 (4 sccm) /Ar (25 sccm). By using ICP PECVD, we deposited, Si_xN_y thin films having impurities such as oxygen and hydrogen. For an oxygen impurity, an increase in the d.c. bias voltage changed the binding states of the oxygen impurity in the film from Si-O to Si-OH, which were caused by enhanced hydrogenion bombardment, and changed the oxygen content in the film (highest at –50 V). The deposited films were in compressive stress, and a decrease in the oxygen contents and a change in the oxygen binding state from Si-O to Si-OH appeared to decrease the stress in the film. An increase in the d.c. bias voltage increased the hardness and decreased the surface roughness by increasing the density of the film and by increasing the surface mobility of the deposited atoms, respectively. A significant improvement in the film's density and surface, in addition to a much higher deposition rate, could be obtained by biasing at –100 V.

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REFERENCES

[1] H. Lin, L. Xu, X. Chen, X. Wang, M. Sheng, F. Stubhan, K. H. Merkel and J. Wilde, Thin Solid Films **333**, 71 (1998).
[2] J. Y. Lee and S. H. Lee, J. Korean Phys. Soc. **45**, 558 (2004).
[3] J. H. Lee, C. H. Jeong, J. T. Lim, V. A. Zavaleyev, K. S. Min, S. J. Kyung and G. Y. Yeom, J. Korean Phys. Soc. **48**, 1 (2006).
[4] M. H. Choo, W. S. Hong and S. Im, Thin Solid Films **420-421**, 492 (2002).
[5] M. C. Hamilton, S. Martin and J. Kanicki, IEEE Transactions on Electron Devices 51, (2004).
[6] B. Karunagaran, J. P. Jeong, S. Nagarajan, S. J. Chung and E.-K. Suh, J. Korean Phys. Soc. **48**, 1250 (2006).
[7] S. J. Kyung, M. Voronko, J. H. Lee and G. Y. Yeom, J. Korean Phys. Soc. **47**, 818 (2005).
[8] N. Jehanathan, B. Walmsley, Y. Liu and J. Dell, J. Alloys Compd. **437**, 332 (2007).

[9] L. Jiang, X. Chen, X. Wang, L. Xu, F. Stubhan and K. Merkel, Thin Solid Films **352**, 97 (1999).

[10] N. C. da Cruz, E. C. Rangel, J. Wang, B. C. Trasferetti, C. U. Davanzo, S. G. C. Castro, M. A. B. de Moraes, Surf. Coat. Technol. **126**, 123 (2000).

[11] W. Liao, C. Lin and S. Lee, Appl. Phys. Lett. **65**, 2229 (1994).

[12] J. H. Kim and K. W. Chung, J. Appl. Phys. **83**, 5831 (1998).

[13] J. Viard, E. Beche, D. Perarnau, R. Berjoan and J. Durand, J. Eur. Ceram. Soc. **17**, 2025 (1997).

[14] T. Bakos, S. N. Rashkeev and S. T. Pantelides, Phys. Rev. Lett. **88**, 5 (2002).

[15] A. J. Flewitt, A. P. Dyson, J. Robertson and W. I. Milne, Thin Solid Films **383**, 172 (2001).

[16] D. S. Wuu, W. C. Lo, C. C. Chiang, H. B. Lin, L. S. Chang, R. H. Horng, C. L. Huang and Y. J. Gao, Surf. Coat. Technol. **198**, 114 (2005).

[17] B. S. Sahu, P. Srivastava, H. K. Sehgal and O. P. Agnihotri, Thin Solid Films **415**, 53 (2002).

[18] M. S. Haque, H. A. Naseem and W. D. Brown, J. Appl. Phys. **81**, 3129 (1997).

[19] R. K. Pandey, L. S. Patil, J. P. Bange, D. R. Patil, A. M. Mahajan, D. S. Patil and D. K. Gautam, Opt. Mater. **25**, 1 (2004).

[20] R. Gonzalez-Luna, M. T. Rodrigo, C. Jimenez and J. M. Martinez-Duart, Thin Solid Films **317**, 347 (1998).

[21] X. Li and B. Bhushan, Mater. Charact. **48**, 11 (2002).