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Thick SiO_2 Films Obtained by Plasma-Enhanced Chemical Vapor Deposition Using Hexamethyldisilazane, Carbon Dioxide, and Hydrogen

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Amorphous silicon dioxide thick films were prepared on glass and silicon substrates by plasma-enhanced chemical vapor deposition using hexamethyldisilazane H_2, and CO_2, where the H_2 acted as a reactant and carrier gas. These films were studied by choosing different substrate temperatures, radio frequency (rf) discharge power, and flow rates of H_2 and CO_2. A variation in the heat of adsorption with rf power was identified. The films were characterized by electron spectroscopy for chemical analysis and scanning electron microscopy. The growth rate increased with rf power, but decreased with increasing substrate temperature. An adsorption-controlled reaction was identified in this system with a varying heat of adsorption depending on the rf power. Hardness changed with experimental parameters and varied in the range of 10-16 GPa. Scratch tests showed a brittle fracture of the thick films. The internal stress of the thick films was determined for different deposition parameters. Refractive indices of the thick films also were measured and varied in the range of 1.33-1.61.

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Thick silicon dioxide (SiO_2) films have become important due to their applications in the integration of optical and microelectronic devices[1-3] and optical devices,[4,5] in addition to their wide application as the interlevel dielectric in metal oxide semiconductor devices. The role of SiO_2 as a buffer layer material in optoelectronic devices requires a film thickness greater than 3 μm to minimize light absorption by the silicon substrate.[6] However, thick SiO_2 films generally have high stress that causes the films to crack and peel.[7]

Plasma-enhanced chemical vapor deposition (PECVD) offers a lower deposition temperature and higher deposition rate by plasma assistance than the higher deposition temperature and lower deposition rate required in conventional CVD. Furthermore, PECVD can yield films with lower thermal stress and better adherence without the film cracking and peeling.

The main reactant systems for depositing thick SiO_2 films by CVD methods are SiH_4-O_2, [8,9] SiH_4-N_2O,[10,11] tetraethoxysilane (TEOS),[12] and TEOS-O_3.[13,14] SiO_2 films of up to ~10 μm thick at a high deposition rate of ~3 μm/h were recently deposited by Alayo[2] using PECVD and the (N_2O + SiH_4) gas system. Bulla and Morimoto[3] combined PECVD and rapid thermal annealing (RTA) to deposit SiO_2 films with a thickness of ~ 4 μm. Haque *et al*. also produced thick SiO_2 films at a deposition rate of ~6 μm/h by PECVD.[4]

Hexamethyldisilazane [$(CH_3)_3Si$-NH-$Si(CH_3)_3$, HMDSN] is a suitable source for CVD reactions due to its low cost, high vapor pressure, and safety. This reactant has been used for amorphous SiC:H films by plasma-polymerization,[15] for silicon dioxide in an oxygen plasma,[16] for SiO_xN_y in a NH_3 + O_2 plasma,[17] and for Si(C,N) by plasma nitriding.[18] However, its wide application in the semiconductor and optoelectronic industry remains yet unexplored.

In this work, PECVD was used to prepare thick SiO_2 films using a gas mixture of HMDSN, CO_2 and H_2. The effects of process parameters on the deposition kinetics, composition, mechanical properties of hardness, elastic modulus, scratch adhesion, and internal stress, and refractive index were the focuses of this study.

Experimental

SiO_2 coatings were prepared in a 13.56 MHz radio frequecy (rf) PECVD reactor. The setup of this deposition system was schematically presented in a previous publication.[18] The substrate is placed on the lower electrode which has rf power applied to it, while the upper electrode, used as a gas shower, is grounded.

The deposition parameters for the SiO_2 films are summarized in Table I. The complex reaction sources include HMDSN, H_2, CO_2, and Ar. The selection of CO_2 instead of O_2 for an oxygen source is based on safety reasons and a rapid reaction between CO_2 and H_2 to form CO and H_2O. H_2 flowed in two lines, one for carrying the HMDSN and the other for controlling the total H_2 input. The flow rate of HMDSN was controlled by adjusting the evaporator temperature at 25°C under a constant carrier H_2 flow rate of 100 standard cubic centimeters per minute (sccm). The flow rates of H_2, CO_2, and Ar were measured with calibrated mass-flow meters. The chamber was under a pressure of 5 Torr during deposition. The total flow rate was controlled at 270 sccm. Inert Ar gas was introduced in each experiment to keep the total flow rate constant, to maintain the growth kinetics consistent in different experiments. Silicon wafer and Corning 1737 glass were the chosen substrates.

Film thickness and internal stress were measured by a Tencor P-1 profiler. Crystal structures were analyzed using X-ray diffraction (XRD, Bruker D8, Germany). Scanning electron microscopy (SEM, Hitachi S-3500H, Japan) was used to observe the morphology of the coating, while electron spectroscopy for chemical analysis (ESCA, Physical Electronics PHI 1600, USA) was used to analyze the composition of the films. The internal stress was estimated from the change in the curvature of the substrate/film system using the Stoney formula.[19] The curvature was obtained through the profiler measurement. A Fischer's FURH 100 nano-indenter with loading increased from 0.4 to 100 mN at a 0.24 mN step was used to measure the hardness. A scratch testing machine (Quad group: Romulus III, USA) was employed to evaluate adhesion between the film and the glass substrate. The final load was 60 N. The onset of peeling was monitored by optical microscopy to determine the critical load. An ellipsometer (Rudolph Research Analytical, auto EL III-REV 304, USA) was applied to measure the refractive index at an 830 nm wavelength.

Results and Discussion

Growth behavior of thick silicon dioxide films.—Figure 1 shows the growth rate dependence on the substrate temperature and flow

Table I. Deposition conditions for the silicon dioxide film synthesis.

Substrate temperature	300-450°C
Chamber pressure	5 Torr
RF discharge power	50-200 W
HMDSN vaporizer temperature	25°C
H_2 total gas flow rate	170-220 sccm
CO_2 gas flow rate	30-70 sccm
Ar gas flow rate	0-50 sccm
Total gas flow rate	270 sccm

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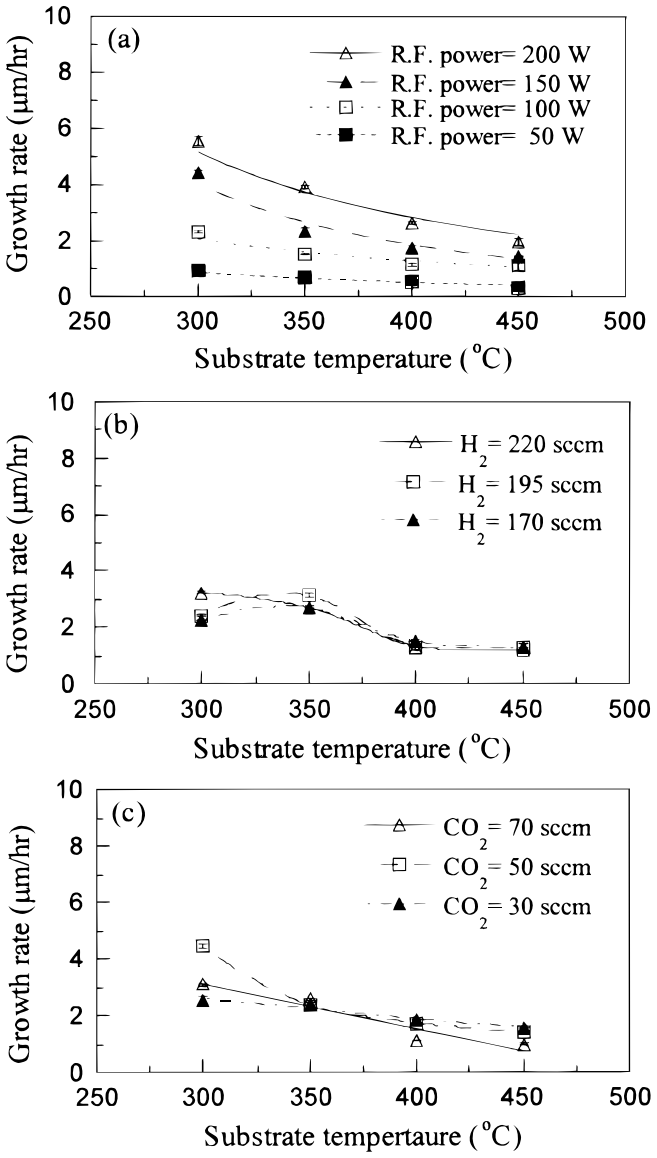

Figure 1. The dependence of growth rate of the SiO_2 films on the deposition temperature at different (a) rf powers (total H_2 flow rate 200 sccm, CO_2 flow rate 50 sccm), (b) total H_2 flow rates (rf power 150 W, CO_2 flow rate 50 sccm), and (c) CO_2 flow rates (rf power 150 W, total H_2 flow rate 200 sccm).

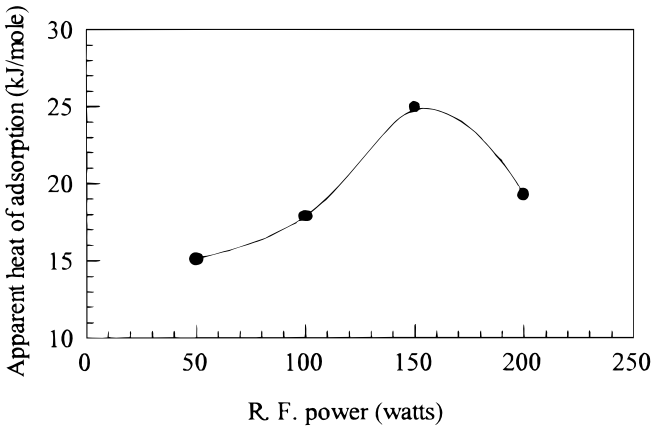

Figure 2. Variation of the apparent heat of adsorption of the SiO_2 films with rf power (total H_2 flow rate 200 sccm, CO_2 flow rate 50 sccm).

rates of H_2 and CO_2. The growth rate ranged from 0.3 to 5.5 μm/h (Fig. 1a). The growth rate decreased with increasing substrate temperature and increased with increasing rf power. Thick SiO_2 films in this study are deposited by PECVD, similar to previous studies.[1-3] The introduction of CO_2 and H_2 to form H_2O and CO possibly favors the formation of thick films under a plasma state with little concern of film cracking. The effect of substrate temperature on the growth rate increased as the rf power increased. However, the growth rate changed very little with substrate temperature at a low rf power of 50 W. The decrease in deposition rate with increasing substrate temperature is characteristic of an adsorption-controlled reaction,[20-22] At high substrate temperatures, the probability for desorption is high and the net deposition rate decreases. However, the reaction is limited by the number of active species created in the discharge at low rf power. Increasing the power increases the number of active species and, consequently, increases the deposition rate. The apparent heats of adsorption, calculated by least-squares regression fitting of an Arrhenius equation to the data in Fig. 1a, are between 15 and 25 kJ/mol as shown in Fig. 2. The heat of adsorption is low compared to the values of 37.7(9)-54.4 kJ/mol (13 kcal/mol) reported for the deposition of silicon dioxide using the tetraethoxysilane reaction.[20] The heat of adsorption in this study is a function of rf power and increases with rf power to a maximum of 25 kJ/mol at 150 W, but decreases to 19 kJ/mol at a higher rf power of 200 W. The decrease in heat of adsorption at 200 W can be related to the higher ion bombardment of the substrate which causes the adatoms to escape easily. The growth rate was independent of the flow rates of H_2 and CO_2, as shown in Fig. 1b and c, respectively, but decreased slightly with increasing substrate temperature.

Characterization of thick silicon dioxide films.—The as-deposited SiO_2 films formed in the temperature range of 300 to 450°C are essentially amorphous, as determined by XRD analysis. A cross-sectional view of an SiO_2 film is shown in Fig. 3. Most films obtained in this study have a similar morphology, *i.e.*, a uniform, smooth, and dense microstructure.

Compositional analysis of the SiO_2 films was performed by ESCA, and the amounts of Si, C, N, and O elements were determined. A plasma precleaning step was performed before the ESCA analysis. Figure 4 shows the compositional dependence of the thick SiO_2 films on the rf power, substrate temperature, and CO_2 flow rate. The deposited SiO_2 had a composition in the range of 30-33% for Si, 51-62% for O, 6-14% for C, and <3% for N. The film composition remained essentially unchanged for different rf powers except for a low rf power of 50 W, where the amount of the O element is slightly lower and the amounts of the other elements are higher than for higher rf powers (Fig. 4a). The lower rf power apparently does not

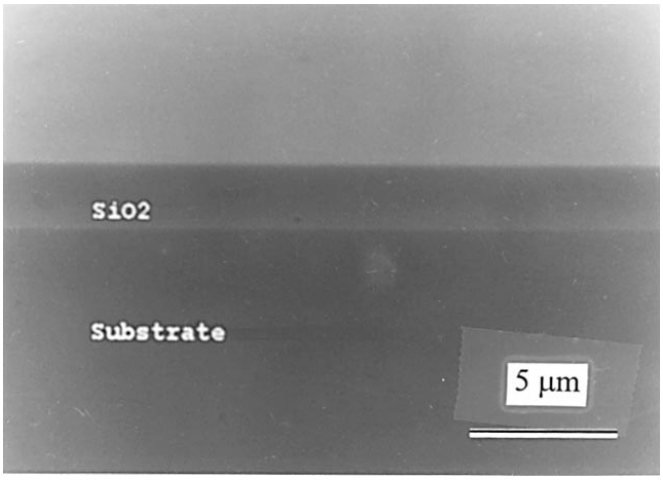

Figure 3. A cross-sectional view of a typical SiO_2 film.

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provide sufficient excitation energy to completely dissociate the reactant gases. Furthermore, the film composition of the thick SiO_2 deposits also remained unchanged with variation of the CO_2 flow rate at different deposition temperatures (Fig. 4b). From the above results, it can be concluded that the HMDSN-H_2-CO_2 reaction system in PECVD can easily produce films with a constant composition and low impurity content.

Properties of thick silicon dioxide films.—Hardness test.—The surface hardness of the SiO_2 films depends on the deposition parameters. Figure 5a-c shows the variation of hardness with rf power, and with flow rates of H_2 and CO_2 at different substrate temperatures, respectively. The hardness values measured by a nano-indenter varied from 10 to 16 GPa, depending on the process conditions. Hardness increases with increasing substrate temperature, as shown in Fig. 5a, but starts to decrease as the deposition temperature exceeds 400°C. Hardness also decreased with increasing rf power (Fig. 5a). However, H_2 flow rate in the range of 170-220 sccm had little effect on the hardness, while it decreased as the CO_2 flow rate increased from 30 to 70 sccm. (Fig. 5b and c).

The heterogeneous deposition reaction is enhanced by increasing the plasma parameters, *e.g.*, the discharge output power and pulse duration, and the substrate temperature, and therefore, improves the mechanical properties,[23] *e.g.*, hardness and adhesion. Another important parameter is the deposition rate. With increasing deposition rate, the hardness and adhesion decrease.[23] In our previous study,[18] the measured hardness of the PECVD Si(C,N) deposits increased with rf power and with deposition rate, which was not consistent with the results of Rie *et al.*.[23] In this study, however, hardness decreases with increasing deposition rate or decreasing deposition temperatures, but decreases with increasing rf power (Fig. 5a). The contradiction is related to the reactant species and their reaction on the substrate surface. It is expected that a higher rf power enhances the ionization of reactants. The intense ionization can promote the deposition reactions among reactants of HMDSN, H_2, and CO_2 to form the SiO_2 films. However, a lower rf power cannot produce complete reactions; therefore, an amorphous SiO_2 film with more Si-C or Si-N results, which has a higher hardness. The Si-C and Si-N bonds have less chance to form at deposition temperatures exceeding 400°C. For this reason, the hardness increases with increasing deposition temperatures up to 400°C, but starts to decrease above 400°C (Fig. 5a). For the nonoxide system of PECVD Si(C,N), the intense ionization and ion bombardment at higher rf powers intensify the decomposition of reactants to form a dense deposit with a higher hardness. This explanation can be elucidated by the compositional analysis, as shown in Fig. 4a, where excess C exists in the film deposited at a low rf power of 50 W. One conclusion is that the relation between the hardness and rf power also is related to types of chemical reactions in the PECVD system. A consistent result is that a film

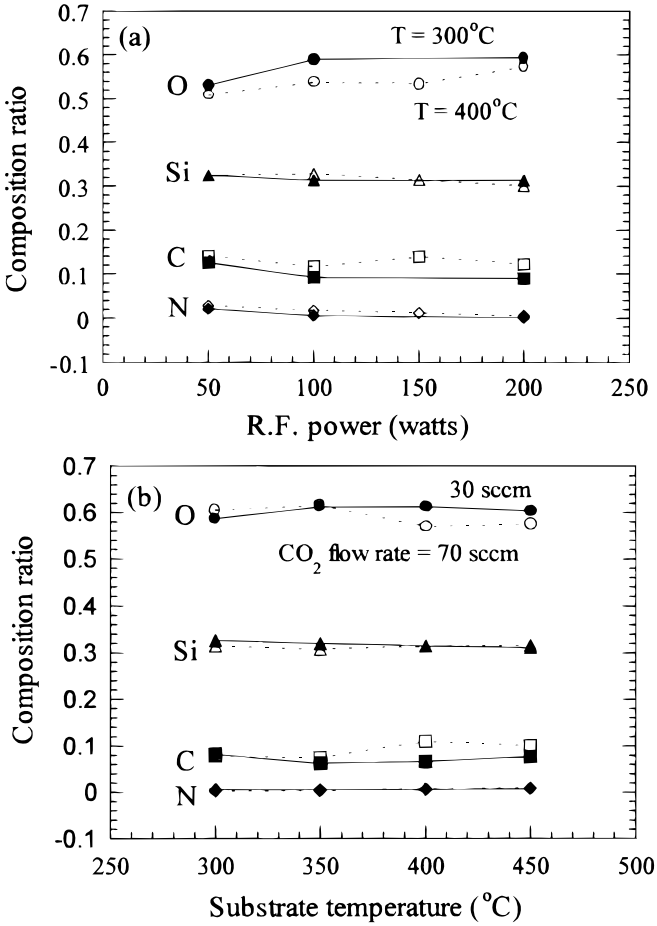

Figure 4. Compositional dependence of the thick SiO_2 films on (a) the rf power at different substrate temperatures (total H_2 flow rate 200 sccm, CO_2 flow rate 50 sccm) and on (b) the substrate temperature at different CO_2 flow rates (rf power 150 W, total H_2 flow rate 200 sccm).

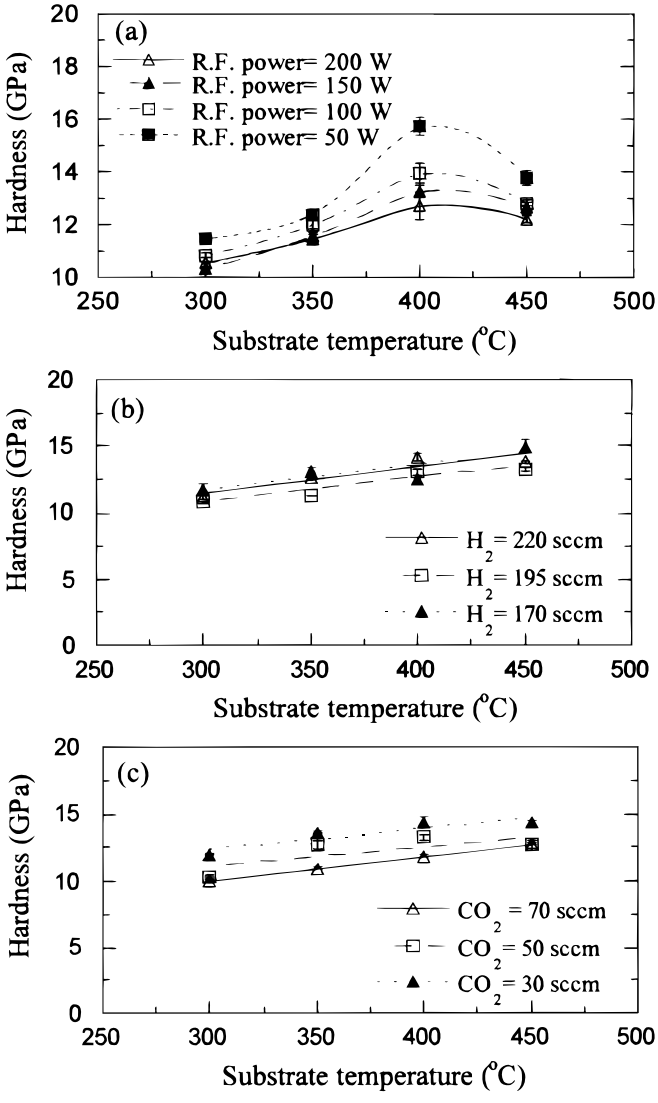

Figure 5. Dependence of the hardness of the SiO_2 films on the deposition temperature at different (a) rf powers (total H_2 flow rate 200 sccm, CO_2 flow rate 50 sccm), (b) total H_2 flow rates (rf power 150 W, CO_2 flow rate 50 sccm), and (c) CO_2 flow rates (rf power 150 W, total H_2 flow rate 200 sccm).

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with a higher growth rate possesses a lower hardness. Furthermore, hardness consistently decreases with increasing CO_2 flow rate, as seen in Fig. 5c. Although a higher CO_2 input possibly could produce more Si-O bonds and lower the hardness, the compositional analysis in Fig. 4b does not fully support this situation. The effect of CO_2 flow rate on hardness possibly involves other factors, *e.g.*, growth rate, film quality. A hardness value of a pure SiO_2 coating is reported as 11 GPa,[19] which is consistent with the results in this study.

Internal stress.—The internal stress in deposited thick films mainly originates from plasma bombardment[24,25] and the mismatch in coefficients of thermal expansion (CTEs) of the film and substrate. The internal stress is composed of two components; *i.e.*, intrinsic and thermal. The intrinsic stress is caused by the bonding structure and its chemical bonding with and its nucleation on the substrate.[26] The thermal component is caused by the difference in CTEs of the substrate and the film. From the viewpoint of processing, the internal stress depends on the substrate temperature, gas composition, pressure, power, and frequency.[24,25,27] These factors influence the film properties and quality. The substrate chosen for this study was a silicon wafer with a CTE value of 2.3×10^{-6}/°C. All the films were in compressive stress due to the smaller CTE of SiO_2 (0.55×10^{-6}/°C). The dependence of the internal stress in the thick SiO_2 films on the rf power and substrate temperature is shown in Fig. 6a. The compressive internal stress is in the range of 400-800 MPa. The stress in plasma silicon dioxide is tensile[3] or compressive.[28-30] depending on the process conditions. The compressive stress usually ranges from 100 to 300 MPa. The higher compressive stress in this study can be attributed to the film composition, higher deposition temperatures, and the rf power. Changes in the H_2 and CO_2 flow rates did not have a strong effect on internal stress. The dependence of the internal stress on rf power showed a minimum at 100 and 150 W for substrate texmperatures of 300 and 400°C, respectively. The increase in film thickness with increasing rf power decreases internal stress.[27] In addition to the increase in growth rate, the increased power also increases ion bombardment of the substrate and the internal stress in the films. Therefore, a minimum internal stress is obtained at an rf power where the effects of the growth rate and ion bombardment cancel each other. Also, the slight increase in internal stress with increasing substrate temperatures can be explained by the effect of the growth rate. The H_2 and CO_2 flow rates have little effect on the internal stress. A slight deviation of the internal stress at a CO_2 flow rate of 30 sccm can cause insufficient supply of the oxygen element and lead to the change of intrinsic stress due to chemical bonding at different process parameters.

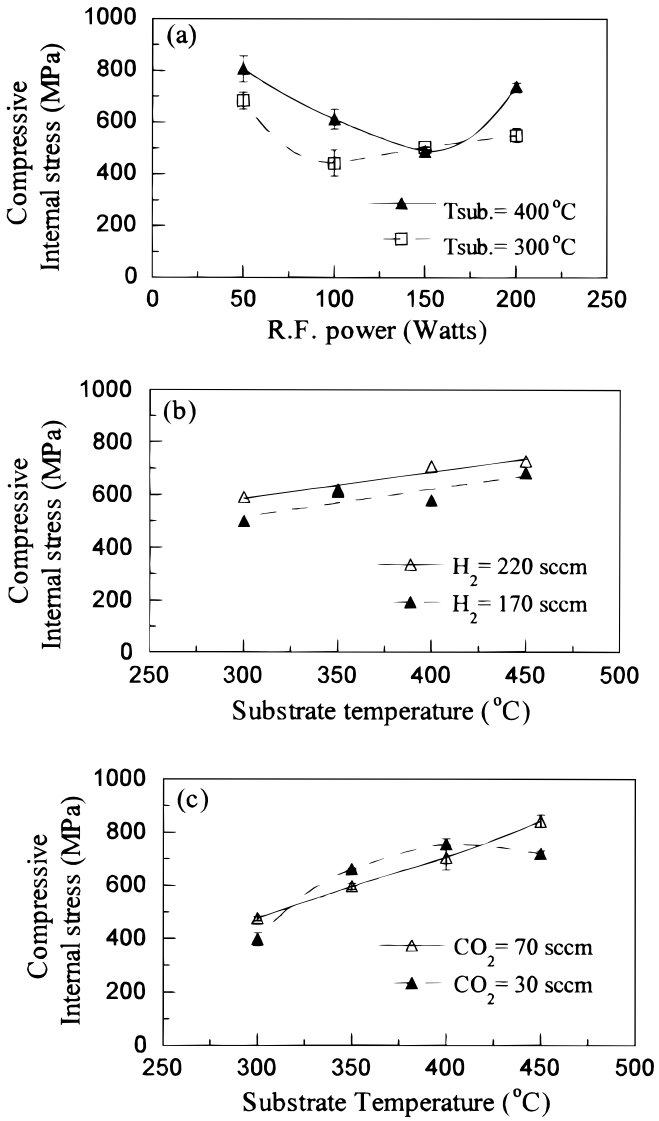

Figure 6. Variation of the internal stress of the SiO_2 films with (a) rf power at different substrate temperatures and with substrate temperature at different (b) total H_2 flow rates (rf power 150 W, CO_2 flow rate 50 sccm) and (c) CO_2 flow rates (rf power 150 W, total H_2 flow rate 200 sccm).

Scratch adhesion test.—The normal force that produces coating failure by the scratch test is known as the "critical normal force," $F_{N,C}$, and is used as a measure of the adhesion. In this study, the tests were executed on thick SiO_2 films with thick Corning glass plates as the substrate instead of silicon wafers to prevent cleavage fracture of the substrate. Figure 7 shows the coating failure resulting from a scratch test for the SiO_2 films deposited on a Corning 1737 glass plate. After reaching the critical load, the SiO_2 film in Fig. 7 shows brittle cracking and contains SiO_2 fragments after the scratch head passes by.

The dependence of the critical force on the deposition temperature at different rf powers, total H_2 flow rates, and CO_2 flow rates is shown in Fig. 8a-c. The critical loads were similar at deposition temperatures of 300 and 400°C if the rf power was less than 200 W (Fig. 8a). For most situations, a higher substrate temperature and lower deposition rate improve the adherence property in a plasma deposition system.[5,31] Better adhesion at higher rf power also has been shown and explained by the enhancement of ion bombardment on the biased substrate. However, improved adherence at higher substrate temperatures and lower deposition rates was only observed for depositions at a low rf power of 50 W (Fig. 8a). The adherence was not a strong function of process parameters for rf powers of 100 and 150 W. Furthermore, a higher critical load occurred at higher coating thicknesses or higher deposition rates at an rf power of 200 W, which

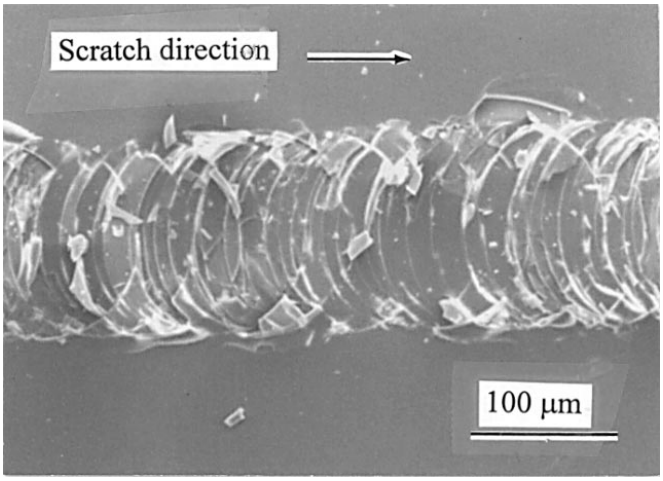

Figure 7. SEM micrograph of a cracked SiO_2 film after a scratch test.

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is consistent with previous observations.[18,32] The critical load ranges from 40 to 50 N. It is comparable with those of Ti(C,N) on metallic substrates[23] and diamond-like carbon films on WC-Co substrates.[33]

The factors influencing the SiO_2 adhesion, measured by scratch tests, are complex since we considered the growth rate, internal stress, composition, and hardness. Although the scratch test can determine the adhesion, the mechanisms involved in the adhesion remain complex. The variation of critical load with process parameters shown in Fig. 8a can be rationalized if the hardness of the films is taken into consideration. Basically, the brittleness increases with increasing hardness. A brittle material is more sensitive to flaw size, which is based on the Griffith criterion.[34] Therefore, a thick film with higher hardness is more sensitive to the contact of a sharp scratch head. Although better adherence should occur for higher deposition temperatures, the tendency to degrade the resistance of the sharp contact gradually changes due to the higher hardness at 400°C.

The critical load also changes slightly with substrate temperature for various H_2 and CO_2 flow rates (Fig. 8b-c). The adhesion improves as the H_2 flow rate increases from 170 to 220 sccm (Fig. 8b). The adhesion also improves as the CO_2 flow rate increases from 30 to 70 sccm (Fig. 8c). The effect of the H_2 and CO_2 flow rates on adherence also can be tentatively explained by the brittleness of thick films, as mentioned previously.

Refractive index.—Figure 9 shows the dependence of refractive index on the process parameters (rf power, substrate temperature, and H_2 and CO_2 flow rates). The refractive index ranges from 1.33 to 1.61. The refractive index remains constant at 300 and 400°C under the conditions of sufficient H_2 (Fig. 9a-b) and CO_2 (Fig. 9c) flow rate regardless of the change in rf power and substrate temperature. The H_2 flow rate had a large effect on the refractive index (Fig. 9b). A higher H_2 flow rate of 220 sccm yielded a constant refractive index of ~1.60, whereas the index was lower and changed with substrate temperatures at a lower H_2 flow rate of 170 sccm with the CO_2 flow rate fixed at 50 sccm.

The refractive index of plasma-deposited silicon dioxide is usually between 1.45 and 1.55,[29,35-37] while it is 1.44-1.46 for chemically deposited silicon dioxide. Most of our results coincide with published data. The higher H_2 flow rate provides a better reduction

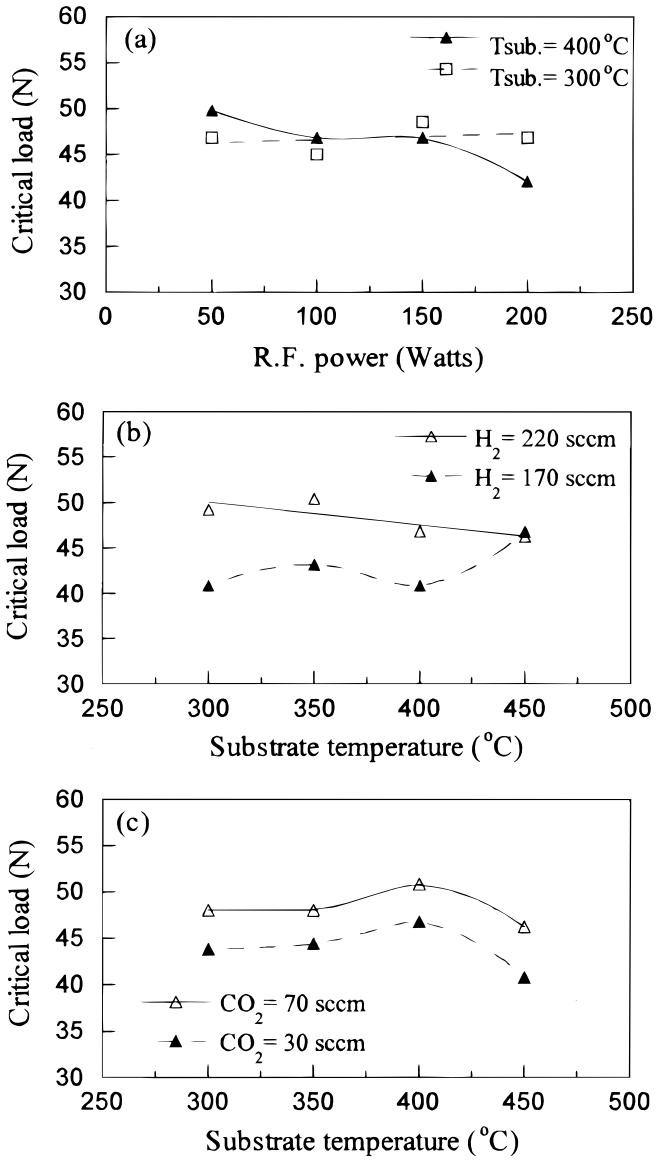

Figure 8. Variation of the critical adhesion load of the SiO_2 films with (a) rf power at different substrate temperatures and with substrate temperature at different (b) total H_2 flow rates (rf power 150 W, CO_2 flow rate 50 sccm) and (c) CO_2 flow rates (rf power 150 W, total H_2 flow rate 200 sccm).

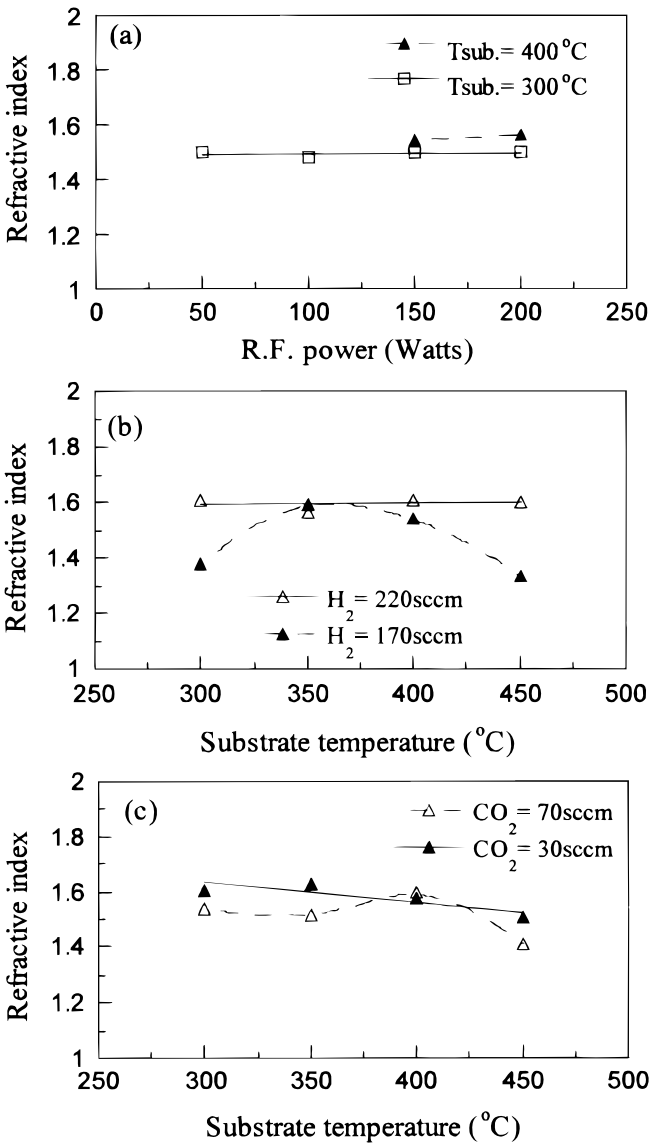

Figure 9. Variation of the refractive index of the SiO_2 films with (a) rf power at different substrate temperatures and with substrate temperature at different (b) total H_2 flow rates (rf power 150 W, CO_2 flow rate 50 sccm) and (c) CO_2 flow rates (rf power 150 W, total H_2 flow rate 200 sccm).

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environment and leaves more Si-C bonds unoxidized. The higher refractive index of ~1.60 occurred possibly due to the existence of Si-C bonds. A lower H_2 input favors the formation of more Si-O bonds, which lowers the refractive index below ~1.60. Nevertheless, the occurrence of a deposit with a refractive index lower than 1.44 (Fig. 9b) can be explained by the existence of defects such as voids, and absorbed H_2O. The CO_2 flow rate also played a role in changing the refractive index (Fig. 9c). Although a higher CO_2 input is expected to enhance the formation of Si-O bonds and produce lower refractive indices, other factors, such as porosity and impurity, may also have an effect.

Conclusions

Thick SiO_2 films were successfully deposited by PECVD using hexamethyldisilazane, hydrogen, and carbon dioxide as reactants. The growth behavior of a decreasing deposition rate with increasing substrate temperature is a characteristic of an adsorption-controlled reaction. The film thicknesses ranged from 0.3-5.5 μm, or a growth rate of 0.3-5.5 μm/h . The heat of adsorption was estimated to be in the range of 15-25 kJ/mol with a maximum at an rf power of 150 W. The flow rates of H_2 and CO_2 had a slight effect on the growth rate of the SiO_2 films. The composition characterization of the deposits, examined by ESCA, revealed the Si content to be 30-33%, the O content to be 51-62%, the C content to be 6-14%, and the N content to be less than 3%.

The hardness values varied from 10 to 16 GPa depending on the process conditions. Hardness increased with increasing substrate temperature, but started to decrease for deposition temperatures higher than 400°C. Hardness also decreased with increasing deposition rate and rf power. A H_2 flow rate in the range of 170-220 sccm had little effect on the deposition rate, while the hardness decreased as the CO_2 flow rate increased from 30 to 70 sccm. The critical load changed slightly with substrate temperature and rf power. The internal stress was in the range of 400-800 MPa. The changes in the H_2 and CO_2 flow rates did not have a big effect on internal stress. The dependence of the internal stress on the rf power showed minima at 100 and 150 W for substrate temperatures of 300 and 400°C, respectively. The adhesion improved as the H_2 and CO_2 flow rates increased. The refractive index of the deposited SiO_2 was in the range of 1.33-1.61.

Acknowledgments

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