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A study on electrical and mechanical properties of hybrid-polymer thin films by a controlled TEOS bubbling ratio

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ABSTRACT

Organic–inorganic hybrid-polymer thin films were deposited on silicon(1 0 0) substrates at room temperature by PECVD (plasma enhanced chemical vapor deposition). Ethylcyclohexane and TEOS (tetraethoxysilane) were utilized as organic and inorganic precursors with hydrogen gas for the ethylcyclohexane bubbler and argon gas for both the TEOS bubbler and as a carrier gas. To compare the electrical and the mechanical properties of the plasma polymerized thin films, we grew the hybrid-polymer thin films under conditions of various TEOS bubbling ratios. MTS nano-indenter was used to measure the hardness and Young's modulus and showed that these values increased as the TEOS bubbling ratio increased, with the highest hardness at 0.8 GPa in this experiment. An impedance analyzer was utilized for the measurements of *I–V* curves and capacitance, showing the lowest dielectric constant at approximately 1.83, with a leakage current density of 10^{-8} A/cm^2 at 1 MV/cm, respectively.

1. Introduction

Advances in the performance of ULSI (ultra large scale integrated) have been hindered in recent years by difficulties with the introduction of materials in the interconnect portion of the Si chip technology. A large effort was invested for many years to replace the SiO_2 dielectric with materials having a significantly lower dielectric constant [1] because the problems of propagation delay, cross-talk noise, and power dissipation, due to resistance–capacitance (R–C) coupling, become significant as a result of increased wiring capacitance, especially interline capacitance between the metal lines on the same metal level. Whereas the resistance is affected by conducting materials, the capacitance is mainly determined by dielectric materials [2]. The use of advanced inter-metal dielectrics to reduce the capacitance seems to be more important than the decrease in resistivity achieved by the substitution of aluminum with copper [3]. Therefore, thin films with relatively low dielectric constants ($k < 3.0$) are under intense study due to their potential application as interlayer dielectrics. Polymer thin films are also considered as possible candidates for low-*k* materials due to their low-*k* values [4]. In order to fulfill the process compatibility and endure the desired electrical performance and high device reliability in end-use, low-*k* materials need to meet a demanding list of electrical, chemical, mechanical, and thermal requirements [5], as well as have a low dielectric constant.

Both organic and inorganic materials are not ideal in at least one important criterion for application. For example, inorganic systems lack sufficient extension to lower the dielectric constant, whereas organic dielectrics do not meet mechanical requirements, especially when considering their inclusion into production schemes with mechanically rigorous integration steps, such as chemical–mechanical polishing. Accordingly, hybrid-polymer thin films with both organic and inorganic components are very promising as low-*k* dielectric materials [6].

In this study, we investigated the influence of the TEOS ratio for electrical and mechanical properties of as-grown, organic–inorganic hybrid-polymer thin films.

2. Experimental

Silicon(1 0 0) wafers were cleaned by sonication with acetone, methyl alcohol, distilled water, and isopropyl alcohol. Substrates were also cleaned by in situ Ar plasma bombardment with 100 W for 15 min. The hybrid-polymer thin films were deposited by PECVD method at room temperature. Ethylcyclohexane and tetraethoxysilane were utilized as organic and inorganic precursor, each preheated at 60 °C and 120 °C, and bubbled with 50 sccm of hydrogen and 5–25 sccm of argon gas, with an additional 50 sccm of argon gas used as a carrier gas. The deposition lasted 25 min to achieve a thickness of 300 nm at a pressure and temperature of 4.0×10^{-1} Torr and room temperature.

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Chemical bonding type of plasma hybrid-polymer thin films was investigated by FT-IR. The MTS nano-indenter was used to measure the hardness and Young's modulus of these films. Measurements were made by applying a constant strain rate to the diamond indenter tip, then unloading the indenter, all while monitoring the load versus total indenter displacement. The hardness and the modulus are continuously determined from load–displacement curves using the continuous stiffness method [7]. Nano-indentation depth is 200 nm. And we already mentioned that each film thickness is 300 nm. Also, nano-indentation results only up to a penetration depth $h \leq$ tf/10 were considered in all analysis, where tf is the thickness of hybrid plasma-polymer film on Si substrate [8]. Also, these films were investigated with MISM (metal–insulator–silicon–metal) structure by a multi-frequency precision LCR meter (HP 4284b) for capacitance and by a semiconductor parameter analyzer (HP 4145B) for I–V curves.

3. Results and discussion

Fig. 1 shows dielectric constants of as-deposition films with RF power. The dielectric constants of 20 and 30 W are almost same, and the dielectric constants linearly increased from 30 to 60 W because crack and pin-hole free hybrid-polymer thin films were made by high RF power as shown in Fig. 2(a) and (b). The RMS roughness value decreased from 1.19 to 0.90 nm with increasing deposition RF power while the AFM images showed the decreasing RMS roughness with an increasing TEOS ratio, Fig. 2(c). The crack and pin-hole of polymer thin film is filled up by a Si–O skeletal structure [9], thus, RMS roughness also decreased from 1.19 to 1.02 nm with an increasing TEOS ratio. It also related with increasing the dielectric constant (Fig. 4). The lowest dielectric constant was 1.83, which was deposited at an RF power of 20 W. From Fig. 1, we investigated the Si ratio-control at 20 W to compare with the electrical and the optical properties of the plasma polymerized thin films and grew the hybrid-polymer thin films under the conditions of various TEOS bubbling ratios.

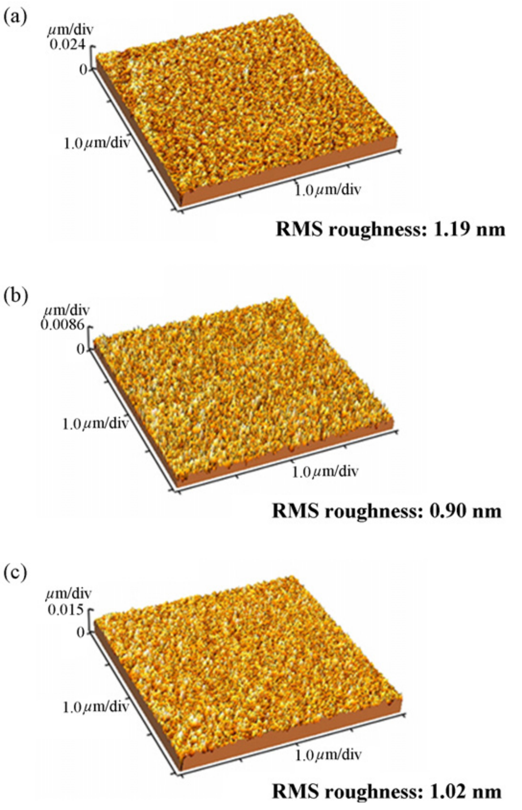

Fig. 2. AFM images and RMS roughness of hybrid films of: (a) 20 W, 1:10; (b) 50 W, 1:10; and (c) 20 W, 4:10.

The bonding state of plasma polymerized thin films was analyzed by FT-IR over the range of 4000–400 cm^{-1} as shown in Fig. 3, on films grown on a Si(1 0 0) substrate as a function of RF power, either at room temperature or annealing temperature. The spectra exhibit an absorption peak at 1050 cm^{-1}, corresponding to the Si–O–C stretching vibration band. Other bands exhibited ranged from 1380–1457, 1722, 2870–2960, and 3300 cm^{-1}, corresponding to CH_x bending vibrations, and C=O, CH_x, and OH stretching vibration bands, respectively. Fig. 3 shows the FT-IR spectra with increasing TEOS flux. These spectra are almost the same with exception to the Si–O–C band (1050 cm^{-1}). As TEOS increased, the shoulder peak of the Si–O band (1100 cm^{-1}) increased, indicating that the Si–O content ratio can be affected by controlling the TEOS bubbling ratio. Thus, the dielectric constant increased by increasing the Si–O ratio because Si–O induces a rise increasing the polarizability of the hybrid-polymer thin films.

Fig. 4 shows the dielectric constants of the hybrid-polymer thin films that grew under 20 W and at different TEOS fluxes. Dielectric constants linearly increased with an increasing TEOS ratio, as it is the sole source of SiO_x and as SiO_2 has a higher dielectric constant ($k = 4.0$) than carbon-based polymers ($k \approx 2.0$). The dielectric constant only changed from 1.83 to 1.91, a difference of only 0.08.

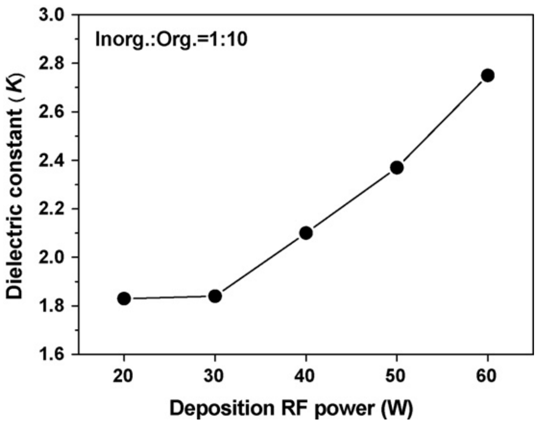

Fig. 1. Dielectric constant of hybrid films with increasing RF power.

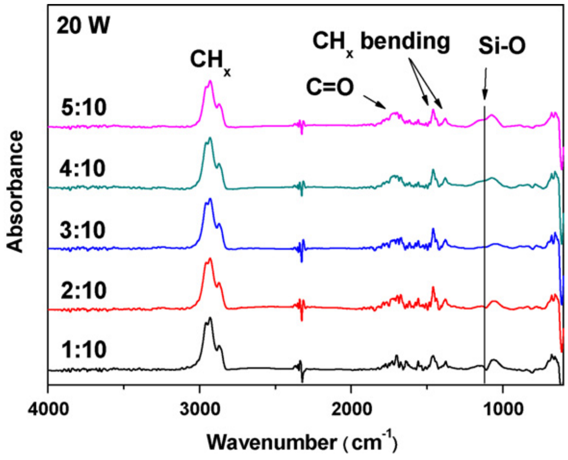

Fig. 3. FT-IR spectrum of hybrid films with increasing TEOS bubbling ratio.

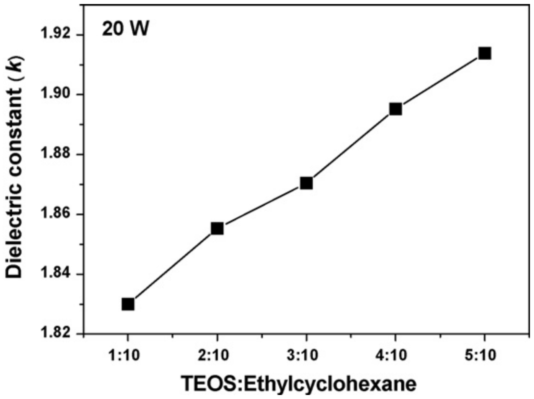

Fig. 4. Dielectric constant of hybrid films with increasing TEOS bubbling ratio.

This increasing phenomenon is, however, lower than by increasing the RF power, where a change in RF power from 20 to 40 W made the difference between dielectric-constants to be 0.3, about 4 times larger than increasing the TEOS ratio. There is an influence of Si ratio and RF power, but, as shown in Figs. 1 and 4, RF power has a larger influence over increasing dielectric constant than the Si ratio does.

Fig. 5 shows the hardness and Young's modulus obtained from the same films shown in Fig. 4. The hardness and Young's modulus have the same increasing tendency as with increasing the TEOS ratio. A hybrid-polymer thin film of 1:10 is not suitable as a low-*k* dielectric because of the low mechanical properties. The hardness increased from 0.38 to 0.85 GPa with increasing the TEOS ratio. Also, Young's modulus increased from 6.52 to 9.51 GPa. The pin-hole of hybrid film filled up with the Si–O skeletal structure, reinforcing the hardness and Young's modulus of the hybrid film. Thus, a high degree of SiO-reinforcement hybrid-film is suitable for a low-*k* dielectric and thus, the hybrid film with Si–O skeletal structure has better mechanical properties than those without the Si–O skeletal structure. Shown in Figs. 4 and 5, increased SiO ratio made two increasing of electrical and mechanical properties. Electrical results showed increasing dielectric constant of 0.08. Mechanical results showed increasing hardness of 0.47 GPa and Young's modulus of 2.99 GPa. The increasing TEOS-ratio affects more mechanical properties than electrical properties.

Fig. 6 shows the leakage current densities of hybrid-polymer thin films with different TEOS ratios, demonstrating that the leakage current densities are not affected to any great extent by increasing the TEOS ratio and the breakdown not appearing below 4 MV/cm. This indicated that our films have a compact structure with high density and pin-hole free layers that are well known to have a lower leakage current density and higher breakdown field [10]. Also, there is no change in leakage current density as there is no change of deposition RF power [11]. The leakage current density of hybrid-polymer thin film is nearly the same because of same deposition RF power. The leakage current density of the hybrid-polymer thin film is shown to be 10^{-8} A/cm^2 at 1 MV/cm.

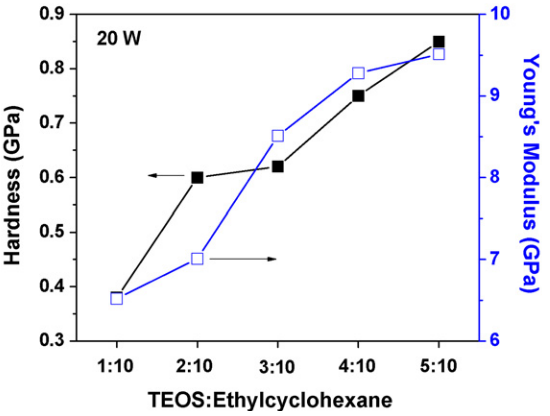

Fig. 5. The hardness and Young's modulus of hybrid films with increasing TEOS bubbling ratio.

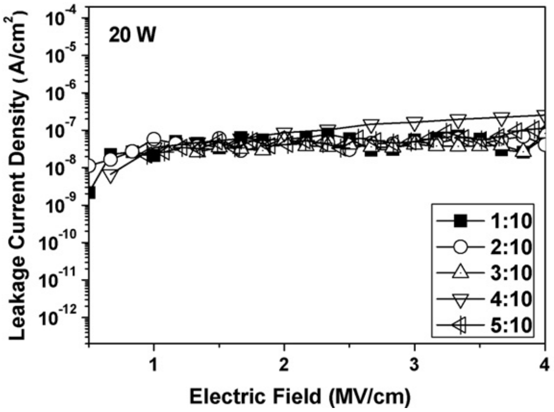

Fig. 6. The leakage current density of hybrid films with increasing TEOS bubbling ratio.

4. Conclusion

The hybrid-polymer thin films were deposited on Si(1 0 0) by PECVD method. Ethylcyclohexane and tetraetoxysilane were utilized as organic and inorganic monomer precursors. FT-IR results showed that the as-grown hybrid films have –CH$_x$, C=O, and SiO$_x$ functional groups, indicating that the thin film has a totally different structure from ethylcyclohexnae and TEOS. These results also showed that hybrid-polymer thin films have a Si–O skeletal structure that increases with an increasing TEOS ratio, which could also be due to increasing the dielectric constant. The dielectric constants increased with increasing the TEOS ratio, but the effect of increasing the TEOS ratio is lower than the effect of increasing the RF power. Also, the hardness and Young's modulus increased with increasing the TEOS flux as the Si–O structure augmented the hardness and elasticity of thin films. A leakage current density of 10^{-8} A/cm^2 at 1 MV/cm occurred at all conditions. As a result, the optimum condition is a TEOS bubbling ratio of 5:10, a hardness and Young's modulus of 0.8 and 9.5 GPa with a dielectric constant of 1.91.

Acknowledgments

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