Characteristics of multilayered plasma-polymer thin films using toluene and TEOS by PECVD

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A B S T R A C T

This study investigated the interaction of alternate multilayer ultralow-k TEOS (tetraethoxysilane)-toluene plasma-polymer thin films, as well as their electrical and chemical properties. Multilayered plasma-polymer thin films were deposited on silicon (1 0 0) substrates with the alternate injection of each precursor at room temperature via the plasma enhanced chemical vapor deposition (PECVD) method. Toluene and TEOS were prepared as the organic and inorganic precursors, and hydrogen and argon gases were used as the bubbler and carrier gases, respectively. To compare differences in the electrical and chemical properties of the multilayer plasma-polymer thin films, the hybrid polymer thin films were grown under 30 W of RF (radio frequency using 13.56 MHz) power with different proportions of toluene and TEOS polymer layer in the same total thickness. The as-grown plasma polymer thin films were first analyzed by using FT-IR (Fourier transform infrared) and FE-SEM (field emission scanning electron microscopy). FT-IR results showed that the hybrid polymer thin films were totally fragmented and polymerized by PECVD. SEM cross sectional images showed alternate TEOS-toluene plasma polymer thin films. Plasma-polymer thin film capacitances were measured to determine the dielectric constant at 1 MHz.

1. Introduction

Recently, there has been increased interest in the use of glow discharge for the polymerization of a number of organic and organometallic compounds [1,2]. Plasma polymers are used as dielectric and optical coating materials to inhibit corrosion. The investigation of the optical properties of polymer films is of particular interest because of their use in optical devices [1]. Among many chemical vapor deposition (CVD) methods, the plasma enhanced CVD (PECVD) process is very efficient for the production of homogeneous organic thin films on large area substrates, offering good control over the film properties [3–7]. Plasma polymerization is a unique method of organic thin film deposition [8].

Advances in the performance of ultra large scale integrated circuits (ULSI) have been hindered in recent years due to difficulties in introducing materials to the interconnect of Si chip technology. As such, a large effort was invested to replace the SiO2 dielectric with materials having a significantly lower dielectric constant [9]. The problems which include propagation delay, cross-talk noise, and power dissipation due to resistance–capacitance (R–C) coupling, became significant due to increased wiring capacitance, especially interline capacitance between the metal lines on the same level. Conducting materials affect the resistance, while, capacitance is mainly determined by the dielectric materials [10]. The use of advanced inter-metal dielectrics to reduce capacitance seems to be more important than the decrease in resistivity provided by the substitution of aluminum with copper [11]. Therefore, thin films with a relatively low dielectric constant (κ < 3.0) are under intense study due to their application as interlayer dielectrics. Polymeric thin films have been considered as possible candidates for low-κ materials [7].

In addition, the mechanical and thermal processing and packaging associated with final chip preparation produce significant stress on the multilevel interconnect structure. Therefore, there are many chemical and physical property requirements which interlayer dielectric (ILD) materials must satisfy in order to be used in current industrial processes. Thermal properties of the dielectric are of particular importance and must be consistent with subsequent processing temperatures and thermal conductivity requirements in order to assure proper heat transfer with a chip. The material should be able to withstand repeated temperature cycling at high temperatures, preferably up to 400 °C, without appreciable weight loss or shrinkage [12].

2. Experimental

The experiment was carried out in a plasma enhanced chemical vapor deposition (PECVD) system. Silicon (1 0 0) wafers were wet-cleaned by using sonication with acetone, methyl alcohol,
distilled water, and isopropyl alcohol. In addition, wet-cleaned substrates were dry-cleaned via in situ Ar plasma bombardment at 100 W for 15 min. Toluene and TEOS were utilized as the organic and inorganic precursors, respectively, with alternating injections. Each precursor was preheated at 60 and 80 °C, and bubbled with 50 sccm of hydrogen and argon, each. An Additional 50 sccm of argon was used as the carrier gas, and the deposition pressure was 4.0 × 10⁻¹ Torr. Additionally, post annealing was carried out to assure the thermal stability of the plasma polymers. The conditions of each sample are shown in Table 1.

The κ values were determined from capacitance measurements in the metal–insulator–silicon–metal (MISM) structure of the Al/hybrid polymer thin film/Si/Al. The capacitance was determined at 1 MHz within the MISM structure. The plasma hybrid-polymer thin film chemical bonding type was investigated by using FT-IR spectroscopy (Bruker Optik, Vertex 70). Layered structures of plasma polymer thin films were measured by using FE-SEM (JEOL, JSM7000F, with the COMPO mode). Surface wettability was measured according to water contact angle measurements (KSV Instruments, attension).

3. Results and discussion

Fig. 1 shows SEM cross-sectional images of the plasma polymer. From the SEM images, the multi-layered plasma polymer thin films were well grown by the PECVD method with alternating injections of toluene and TEOS. Fig. 1b–g show the multilayer plasma polymer thin films and 1(b, d, and e) include COMPO mode SEM images to confirm the structure due to unclear SEM images.

The bonding states of the plasma polymerized thin films were analyzed by FT-IR absorption spectra over a range of 4000–600 cm⁻¹ (Fig. 2). The IR spectra exhibited an absorption peak at 1050 cm⁻¹, corresponding to the Si–O stretching vibration band. Bands ranging from 1375–1444, 1520–1830, 2200, 2800–3000 to 3200–3700 cm⁻¹ corresponded to CHₓ bending vibrations, C = C; C = O, Si–H, CHₓ stretching vibrations, and –OH bands, respectively [13]. The intensities of the CHₓ and SiO peaks changed with
increasing total thickness of the toluene and TEOS plasma polymer layers, respectively.

Fig. 3 shows the contact angle of the plasma polymer. From M1 to M4, the top layer is the toluene plasma polymer layer (called as the toluene group). The top layer of the others (M5–M8) is the TEOS plasma polymer layer (the TEOS group). The contact angles of the toluene group were higher than the TEOS group. Contact angles of the toluene group were $\theta_\text{C24} = 82^\circ$ within the same error range.

And contact angles of the TEOS group were $\theta_\text{C176} = 65^\circ \pm 1.7$. The toluene plasma polymer layer was hydrophobic rather than TEOS plasma polymer layer. Low moisture absorption was expected at high water contact angles. Thus, the anti-moisture performance changed by type of the surface layer, not the thickness of layer. Additionally, the same plasma effect was applied to each layer during the depositions. Thus, surface roughness of the all samples had the almost same value.

Fig. 4 shows the dielectric constant of multi layered plasma polymer thin films. M2 and M7 had the same number of layer. The same as the result in IR, M2 and M7 have similar dielectric constant. Also, M3 and M6, and M4 and M5 had similar dielectric constant, respectively. The different number of organic and inorganic plasma polymer layers resulted in differences in dielectric constant. Additionally, the dielectric constants of the plasma polymer were increased after 1 h of post annealing at 400°C in a vacuum. Except for M2, which had post-annealing dielectric constant of 2.04 all of the samples had dielectric constants greater than 2.5. The dielectric constant of M2 sample is 2.04 after post-annealing.

Fig. 5 shows the thermal shrinkage of the plasma polymer thin films. The thermal shrinkage (%) in all films was dramatically decreased increasing the total thickness of the inorganic plasma polymer layer. M2 and M7 had the same thickness ratio between the organic and inorganic plasma polymers and thus, demonstrated the same thermal shrinkage.

4. Conclusions

Organic–inorganic hybrid-polymer thin films were deposited onto Si(1 0 0) by PECVD method using the alternating-deposition of toluene and TEOS precursor at room temperature.

SEM images showed that the multi-layered plasma polymer thin films were grown by using PECVD method with alternating injections of toluene and TEOS.

IR results showed that the as-grown hybrid thin films had –CH$_x$, C = O, C = C, –OH, and SiO functional groups. Different IR spectra were obtained for each liquid precursor, which also indicated that the thin film between toluene and TEOS was polymerized. Also, the intensity of each peak depended on the total thickness of the organic and inorganic layers.

Contact angle was influenced by type of top layer. The toluene top layer group demonstrated applicable anti-moisture performance more than using the TEOS top layer group.

Similar structures with similar chemical components had similar dielectric constants. However, a multilayered structure cannot be protected from thermal effect in electrical property.

In this study, increasing the inorganic plasma polymer total thickness ratio resulted in increased thermal stability.

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