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Xerogel films have been prepared on *p*-type silicon (pSi) substrates by the sol–gel process using hexamethyldisilazane for surface modification. The dielectric constants of the films are in the range of 1.9–2.5. Detailed electrical characterization has been carried out using an aluminum–xerogel–pSi metal–insulator–semiconductor structure. Low values of fixed oxide charges, mobile oxide charges, and interface state densities have been obtained. The low leakage current density and high breakdown field strength of these films make them suitable for intermetal isolation. Very little degradation of the film properties was observed even after 40 days without any capping layer. [DOI: 10.1063/1.1458065]

As the minimum feature size in integrated circuits continues to shrink toward 100 nm and beyond, delays due to interconnects are increasingly dominating overall gate delays.[1] This interconnect delay depends on the metal resistance and intermetal capacitance. Already copper is replacing aluminum to take advantage of its lower resistivity. The next step will be the substitution of silicon dioxide with insulating films having lower dielectric constants as the interlayer dielectric for on-chip interconnections. A dielectric that holds a lot of promise is SiO_2 based xerogel, which is a porous material having a dielectric constant k in the range of 1.3–2.5, compared to $k=4$ for SiO_2. In addition to its low k, the advantages of xerogel are that it has high thermal stability and can be deposited using the spin-on technique, which has high gap fill properties.

The silica xerogels are prepared by the sol–gel method following a two-step acid base catalyst process.[2] The precursor tetraethylorthosilicate (TEOS) is hydrolyzed by reacting with water with ethanol as the solvent. The hydrolysis reaction is accelerated by HCl, which is the acid catalyst. After hydrolysis, the TEOS undergoes condensation and polymerization, which is accelerated by a base catalyst. The acid-base catalyzed mixture (sol) is then filtered and spun on a silicon wafer in an ethanol-saturated atmosphere. The spun on films are then surface modified and dried at ambient pressure. In the surface modification step, the Si–OH groups on the pore surface, which tend to absorb moisture, are terminated with stable methyl groups. Trimethylchlorosilicate (TMCS) has been widely used for this purpose. The effects of varying extent of surface modification, water to TEOS ratio, and drying temperature on thickness, porosity, and dielectric constant of the xerogel films have been reported by Nitta *et al.*[3] Park *et al.*[4,5] have reported the effects of sol viscosity, aging time, and temperature on the dielectric properties of silica xerogel.

In the present work, hexamethyldisilazane (HMDS) has been used instead of TMCS for surface modification. Both TMCS and HMDS replace the highly polar hydroxyl groups on the surface of the film with less polar methyl groups.[6] However, TMCS contains chlorine and hydrochloric acid (HCl) generated during processing may corrode the metal lines. This is a serious concern for xerogel films to be used as intermetal dielectric in very large scale integrated technology. On the other hand, HMDS does not contain any chlorine and is therefore better suited for this application.

Although there are several reports on the preparation of the xerogel films, the electrical characteristics of these films have not been systematically studied so far. In particular, the properties of the xerogel–silicon interface have not been investigated. In this letter, a detailed study of the passivating properties of xerogel films through current–voltage ($I-V$) and capacitance–voltage ($C-V$) measurements is presented. The values of the fixed oxide charge density Q_f, interface trap density D_{it} as well as the mobile ion density Q_m have been calculated from these measurements. Also, reliability of these films is another important issue. While Schulz *et al.*[6] have studied the effect of different cap layers on HMDS treated xerogel films, in this work the effect of aging on the electrical properties of uncapped films has been studied.

The procedure followed for preparation of the xerogel films is similar to that described by Nitta *et al.*,[3] except that HMDS has been used instead of TMCS for surface modification. It has been reported[4] that the viscosity of the sol increases as a function of time at room temperature and stable xerogel films can be obtained only when the viscosity is in the range of 10–40 cP. In our experiments, the filtrate was left to gel for 10–15 min after base catalysis. Then it was deposited on precleaned *p*-type ⟨100⟩ silicon wafer of resistivity 4–11 Ω cm and spun at 2000 rpm for 12 s. The spun-on film was allowed to gel in ethanol atmosphere for 1 h and then aged in ethanol solution at 50 °C for 24 h. The wafer was then dipped in *n*-hexane to replace ethanol. This was followed by surface modification by immersing the film in 10% HMDS in *n*-hexane for 1 h and curing the film by

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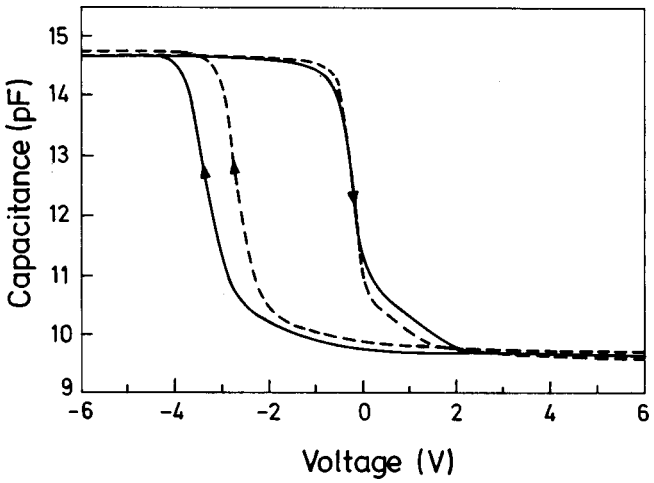

FIG. 1. $C-V$ characteristics of freshly prepared Al–xerogel–pSi MIS device at 1 MHz (solid line) and after aging for 40 days (dashed line).

ramping the temperature from 50 to 450 °C at the rate of 2 °C/min. For electrical characterization, metal–insulator–semiconductor (MIS) capacitors were made by evaporating aluminum (Al) dots of 0.5 mm diameter on the xerogel films. Al was also deposited on the back side of the wafer for the second contact.

The xerogel film thickness t_x was measured by a Dektak 3030 surface profiler. A step was made in the xerogel film for this measurement by etching in buffered hydrofluoric acid (HF) solution. The thickness of the film was found to vary in a wide range of 3000–4900 Å depending on the time the sol was allowed to gel before being spun on the wafer.

Fourier transform infrared (FTIR) spectroscopy of the cured xerogel film pelletized in the KBr matrix was carried out in the range of 400–4000 cm^{-1}. As expected Si–O–Si related peaks were observed in the range 1020–1090 cm^{-1} and peaks of C–H and $-CH_3$ vibrations were observed around 2980, 1385, and 1470 cm^{-1}. However, no peaks due to Si–OH and SiO–H stretching vibrations were observed signifying that HMDS treatment was effective in replacing the surface hydroxyl groups with $-CH_3$. This is in accordance with the results reported previously.[6] FTIR spectrum of films aged for 40 days in ambient conditions (without any capping layer) showed a small broad peak around 3300–3600 cm^{-1} which corresponds to absorbed moisture.

$C-V$ characteristics of a Al–xerogel–pSi MIS structure was obtained using a HP 4275 *LCR* meter at 1 MHz. A typical $C-V$ plot is shown in Fig. 1, which displays well-marked accumulation, depletion, and inversion characteristics. The dielectric constants of the films were calculated from the accumulation capacitance $C_{\max}$ using the measured film thickness data and were found to be in the range 1.9–2.5 depending on the film preparation conditions. The $1/C^2-V$ plot in the depletion region was found to be a straight line with a slope corresponding to a doping concentration of $10^{15}/cm^3$, which matches the wafer specifications. Using the $C-V$ plots, Q_f/q extracted from the flatband voltage[7] was found to be in the range of $8\times10^{10}-1\times10^{11}/cm^2$. D_{it} was also estimated using the high frequency capacitance method developed by Terman[7] and was in the range of $10^{11}-5\times10^{11}/cm^2$ eV with the minima near the middle of the band gap. These values of Q_f/q and D_{it} are quite low for a deposited film and are almost comparable to those obtained for a Si–thermal SiO_2 interface. The $C-V$ plots also displayed a hysteresis in the clockwise direction, probably due to mobile ions. The hysteresis loop has a width (ΔV) of 3 V as seen from Fig. 1. Q_m/q was calculated as $C_{\max}\Delta V/(Aq)$, where A is the area of the MIS capacitor and q is electronic charge, to be equal to $1.38\times10^{11}/cm^2$. In all the films, the Q_m/q values were found to be between $1\times10^{11}/cm^2$ and $1.5\times10^{11}/cm^2$. These values again are very reasonable, considering that the film is prepared using a sol–gel technique, where the solvents may contain ionic impurities. The values of Q_f/q, D_{it}, and Q_m/q are presented in Table I for ready reference. Figure 1 also shows the $C-V$ plot of the same device aged for 40 days. There is only a marginal increase ($<0.5\%$) in the capacitance value showing that the films are quite stable even without any protective layer.

TABLE I. Xerogel film properties obtained from measurements.

Thickness (t_x)	3000–4900 Å
Dielectric constant (k)	1.9–2.5
Fixed oxide charge (Q_f/q)	$8\times10^{10}-1\times10^{11}/cm^2$
Interface state density (D_{it})	$10^{11}-5\times10^{11}/cm^2$ eV
Mobile ion charge (Q_m/q)	$1\times10^{11}-1.5\times10^{11}/cm^2$
Resistivity (ρ)	10^{12} Ω cm
Breakdown field strength	$>10^6$ V/cm

Since the main use of the xerogel film is to provide isolation between metal lines, the insulating property of the film is of paramount importance. The leakage currents of the MIS devices were measured using the HP 4155B semiconductor parametric analyzer. The leakage current density J versus voltage characteristics of the MIS device is shown in Fig. 2. As can be seen, the leakage current density is 2.5×10^{-7} A/cm^2 at 5 V applied bias. The resistivity of the xerogel film ($\rho=V/(Jt_x)$) was calculated to be on the order of 10^{12} Ω cm. This value is smaller than that obtained for SiO_2 films of comparable thickness because of the porous structure of the xerogel films. However, it is still high enough to provide good electrical isolation. Also, the films did not break even when subjected to 40 V, showing a breakdown field strength $>10^6$ V/cm. As shown in Fig. 2, the leakage current was found to increase only slightly after 40

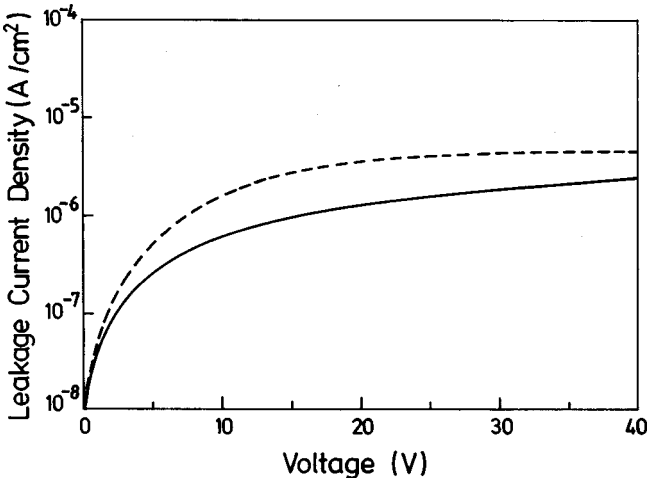

FIG. 2. Leakage current density–voltage characteristics of freshly prepared Al–xerogel–pSi MIS device (solid line) and after aging for 40 days (dashed line).

days of aging, reemphasizing the stable nature of the film.

In summary, low-k xerogel films with dielectric constants in the range of 1.9–2.5 have been successfully deposited on p-Si using the sol–gel technique. HMDS surface treatment has been carried out to terminate the surface with stable methyl groups. FTIR spectra reveal that this surface treatment has indeed been effective in replacing the surface hydroxyl groups with $-CH_3$. Detailed electrical characterization of the films using $C-V$ and $I-V$ measurement of the Al–xerogel–pSi MIS device has been reported, showing low values of fixed oxide charge, interface state density, mobile ionic charge, and leakage current. These values show very little degradation even after 40 days of aging without any capping layer. Thus our results show that the deposited xerogel films are extremely stable and suitable for isolation between metal layers in integrated circuits.

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