



Electrical Stability and Reliability of Ultralow Dielectric Constant Porous Carbon-Doped Oxide film for Copper Interconnect

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Nanoporous carbon-doped oxide (CDO) is a promising low dielectric constant (low- k) intermetal dielectric (IMD) for Cu interconnect. The electrical stability and reliability of CDO strongly depend on the contacted metal. An electrical instability model considering metal ion diffusion, dielectric polarization, and carrier injection is proposed for CDO under electrical stress. Both Al and Cu are not suitable for contact with CDO because they can be driven easily into CDO. Fortunately, TaN shows no mobile ion issues when in contact with CDO. The electron transport mechanism is identified to be Schottky emission at low electric field and low temperature. As metal ions are injected into CDO film, the electron transport mechanism changes to Frenkel-Pool emission at high temperature and high electric field. The injection of metal ions into CDO also degrades the time-dependent dielectric breakdown (TDDB) lifetime of CDO. Fortunately, the commonly used diffusion barrier TaN is an excellent contact metal with CDO. The 1-year-long TDDB lifetime allows an electric field stronger than 2 MV/cm, and the TDDB lifetime at 0.5 MV/cm becomes longer than 10 years by several orders of magnitude. It is concluded that the nanoporous CDO is a very promising IMD for next-generation interconnect systems.

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With the progress of integrated circuit process technology, the feature size is scaled down continuously. As the device performance and the circuit density are improved due to shorter channel length and smaller device geometry, the resistance and capacitance of multilevel interconnect increase due to the thinner metal wires and narrower space between wires. Therefore, the circuit performance becomes limited by the resistance-capacitance delay of interconnect. The currently used aluminum (Al)-based metal wires and the silicon dioxide (SiO₂)-based intermetal dielectric (IMD) are no longer adequate to meet the requirement of multilevel interconnect.¹⁻⁶ New conductors with lower electrical resistivity and new dielectrics with lower dielectric constant are thus inevitable for high-performance ultralarge-scale integrated circuits. At the same time, the current density of metal wires increases and is close to the reliability limitation of Al-interconnect. Higher electromigration resistance becomes another criterion for new conductors. Copper (Cu) and low dielectric constant (low- k) materials are thus selected to replace Al and SiO₂.

The implementation of copper interconnect with a low- k material is the only solution to reduce overall signal delay in the future several technology nodes. The International Technology Roadmap for Semiconductors (ITRS) requests low- k material with an effective k value of 2.3-2.7 in 2007.⁷ Although several porous dielectric materials have been proposed with an acceptable k value,⁸⁻¹⁰ their electrical and thermal stability has not been investigated comprehensively. Recently, metal ion diffusion into porous dielectric film has been reported.¹¹⁻¹⁴ This phenomenon is important for dielectric film electrical stability and reliability. Unfortunately, no literature has addressed this issue until now.

Carbon-doped oxide (CDO) is one of the most promising low- k dielectrics. It can be deposited in a plasma-enhanced chemical vapor deposition (PECVD) system.^{8,15-18} CDO film with good properties of low dielectric constant (~ 2.2), low film stress, high thermal stability, high breakdown field (> 5 MV/cm), and low leakage current had been demonstrated.^{8,19} In this work, we focused on the electrical stability and reliability issues of porous CDO film. The experimental procedure will be explained in the next section. Electrical instabilities are shown in the Results and Discussion section, and a model is proposed to explain the observed instability. Electrical reliability is also evaluated in that section. It is concluded that with suitable

contact metal, porous CDO film is electrically stable and reliable to be used as an IMD for the future two to three technology nodes.

Experimental

Simple metal-insulator-metal (MIS) capacitor structure was used to study the electrical properties of the CDO film. The starting material was phosphorus-doped (100)-oriented 8-in. Si wafer with resistivity of 2-4 Ω cm. To minimize the influence of interface instability, a 10-nm-thick SiO₂ was thermally grown before the deposition of CDO film. The MIS structures are divided into three categories. In the first category, the MIS structure is metal/CDO (200 nm)/SiO₂ (10 nm)/n-Si with various kinds of metal (Al, Cu, TaN, and Pt). These samples are denoted as Al-MIS, Cu-MIS, TaN-MIS, and Pt-MIS. All kinds of metal except Al were deposited in a dc sputtering system while Al was deposited in a thermal evaporating system. The second category is a reference sample with structure of Al (500 nm)/PECVD SiO₂ (30 nm)/CDO (200 nm)/SiO₂ (10 nm)/n-Si and is denoted as Al-MIS-2. Because of the existence of thermal oxide and the work-function difference between gate and Si substrate, the above structures are asymmetric. The third category is an almost symmetric MIS structure using an Al gate and heavily doped n-type Si substrate (less than 0.01 Ω cm). This structure was fabricated to study the carrier transport mechanism. The structure is Al (500 nm)/CDO (200 nm)/n⁺-Si and is denoted as Al-MIS-3. Figure 1 shows the schematic drawings of the structures of the three categories.

Thin CDO film was deposited in a Trikon Technologies Planar 300 plasma-enhanced chemical vapor deposition system at room temperature using an organo-silane precursor with He as carrier gas.⁸ A 30 min nitrogen gas furnace annealing at 400°C was performed before metal gate deposition. A metal mask was used to define gate electrode. A 30-nm-thick SiN_x layer was deposited on the sample surface to protect the dielectric from moisture absorption and to protect the Cu gate from oxidation during storage.

The film thickness and porosity of the deposited CDO film were measured by the ellipsometry method. The atomic composition was determined by Rutherford backscattering spectrometry (RBS) analysis and the major chemical bonds were identified using electron spectroscopy for chemical analysis (ESCA). Fourier-transformed infrared (FTIR) spectroscopy was also employed to evaluate the material property.

Both capacitance-voltage (C - V) and current-voltage (I - V) char-

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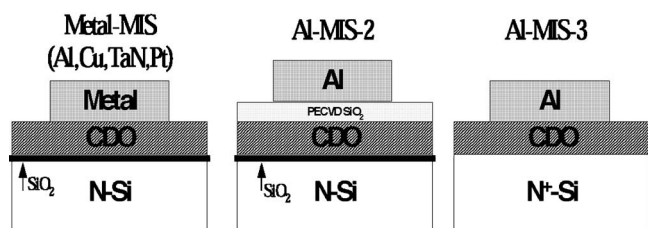


Figure 1. Schematic drawings of the MIS structures used in this work. Metal-MIS: metal/CDO (200 nm)/SiO₂ (10 nm)/n-Si. Al-MIS-2: Al (500 nm)/PECVD SiO₂ (30 nm)/CDO (200 nm)/SiO₂ (10 nm)/n-Si. Al-MIS-3: Al (500 nm)/CDO (200 nm)/n⁺-Si.

acteristics were measured to evaluate the CDO film using a precision impedance meter of model Agilent 4284A and a semiconductor parameter analyzer of model Agilent 4156C, respectively. A bias temperature stress (BTS) test under various temperatures and electric fields was performed. Nitrogen gas purge was carried out during device measurement to avoid moisture absorption and metal gate oxidation. Flatband voltages (V_{FB}) before and after BTS were extracted from high-frequency (100 kHz) C - V characteristic with voltage swept either from inversion mode to accumulation mode [forward voltage sweep (FVS)] or from accumulation mode to inversion mode [reverse voltage sweep (RVS)]. A time-dependent dielectric breakdown (TDDB) test was performed to extract the lifetime of CDO film. CDO dielectric breakdown happened when the stressed capacitor short-circuited.

Results and Discussion

Fundamental properties of CDO film.—Fundamental properties of the CDO film were characterized at first. The dielectric constant of the CDO film calculated from the Al-MIS sample is about 2.2 and apparently reached the level required for the next-generation IMD.⁷ The CDO is composed of Si, C, O, and H atoms and the atomic ratio is Si:C:O:H = 20.5:14.5:31:34. Film volume porosity is about 20% measured by optical ellipsometer with a pore size of 1–4 nm measured by cross-sectional transmission electron microscopy (XTEM).⁸ It would be these nanopores that produce the very low dielectric constant with a low carbon content of 14.5%.

Figure 2a depicts the FTIR spectra of the CDO film after annealing in N₂ ambient at various temperatures. No changes are observed even after annealing at 400°C for 8 h or at 650°C for 30 min. Figure 2b shows that the thickness shrinkage is less than 3% after 650°C annealing, which indicates almost negligible thermal decomposition. The dielectric constant determined by the C - V method increases slightly to 2.3 after annealing at 600°C for 30 min. These results indicate that the thermal stability of CDO is well beyond the requirement of the backend process of the line.

Figure 3a and b shows the current density–electric field (J - E) curves of the Al-MIS-3 capacitors at different temperatures and the breakdown characteristic of Al-MIS-3 capacitors at 200°C, respectively. The CDO film exhibits very low leakage current density of 1 nA/cm² at 2.5 MV/cm and room temperature. It also has very high dielectric strength of higher than 5 MV/cm even at 200°C. It is thus concluded that being a porous low- k material, CDO film shows very good thermal stability and very low leakage current.

CDO electrical instability behaviors.—Although CDO film exhibits low dielectric constant, high thermal stability, low leakage current, and high dielectric strength, electrical instability was observed during the C - V measurement of the Al-MIS sample. By repeating the C - V measurement on the Al-MIS capacitor at room temperature from inversion mode to accumulation mode (FVS) and then from accumulation mode to inversion mode (RVS), V_{FB} shift with respect to the original C - V curve was observed. The C - V curve shifts toward the positive voltage direction under wide-range FVS with voltage sweeps from –40 to 40 V, while it shifts toward the

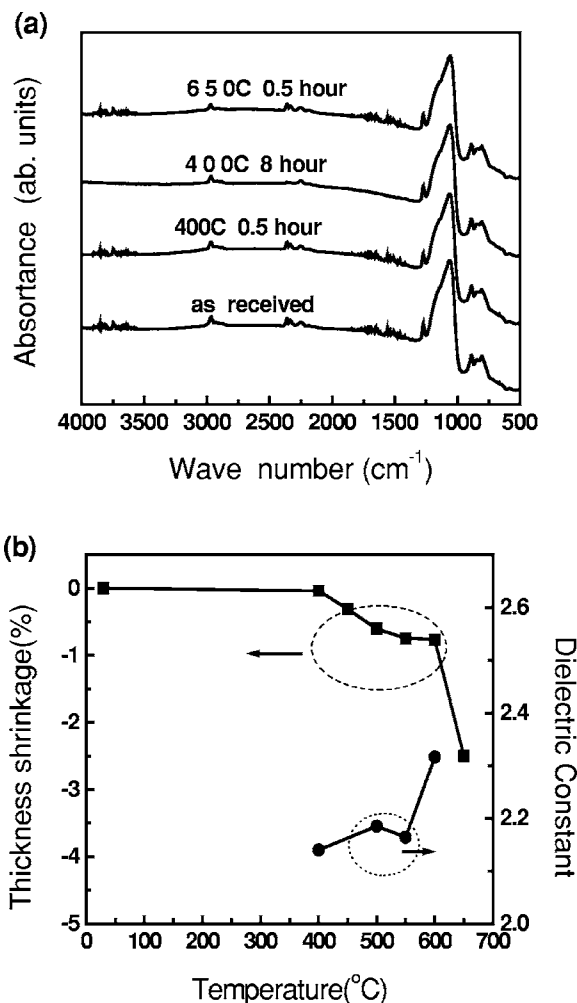


Figure 2. (a) FTIR spectra and (b) thickness shrinkage and dielectric constant variation of CDO film after thermal annealing at different temperatures.

negative voltage direction under wide-range RVS with voltage sweeps from 40 to –40 V. The shifts under FVS and RVS are asymmetric and a net shift toward negative voltage direction was observed. Figure 4 exhibits the C - V curves of the Al-MIS sample before and after electrical stress at –2 and +2 MV/cm for 4 min. It is also observed that positive electric field stress causes larger V_{FB} shift. All of the metal-MIS capacitors exhibit similar electrical instability under continuous C - V measurements. Because of the asymmetric shift, the C - V instability could not be simply explained by the dielectric polarization.²⁰

A BTS test was performed at 30 and 150°C for 30 min. The electric field is 0.6 MV/cm. The magnitudes of V_{FB} shift after BTS are listed in Table I. The magnitudes of V_{FB} shift of the four kinds of MIS capacitors are Al-MIS, Cu-MIS, TaN-MIS, and Pt-MIS in the sequence from high to low. It should be stressed that the magnitude of V_{FB} shift of the Al-MIS sample is even larger than that of the Cu-MIS sample. This observation is totally different from that of the dielectric in silicon dioxide. It is well known that Al is quite stable in contact with SiO₂ because a very thin self-limiting Al₂O₃ forms between Al and SiO₂ and acts as a good diffusion barrier.^{12,13} The TaN-MIS and Pt-MIS samples exhibit very slight V_{FB} shift. As the BTS was performed at 150°C, the magnitude of V_{FB} shift is enlarged but the sequence order remains unchanged.

Dielectric polarization phenomenon of CDO film.—There are four possible mechanisms that may cause dielectric C - V instability: (i) the 10-nm-thick thermal oxide is unstable; (ii) the CDO film is

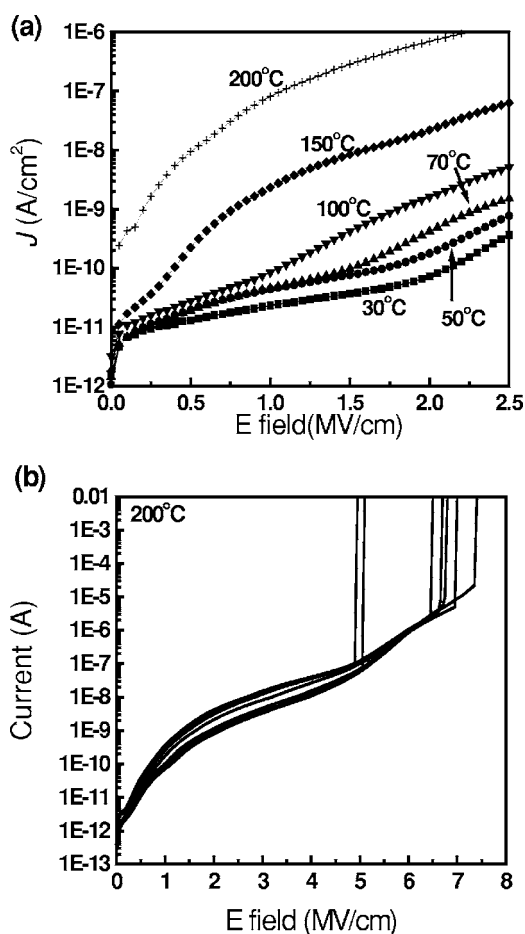


Figure 3. (a) Current density-electric field characteristic of Al-MIS-3 sample measured at different temperatures. (b) The breakdown characteristics of Al-MIS capacitors at 200°C.

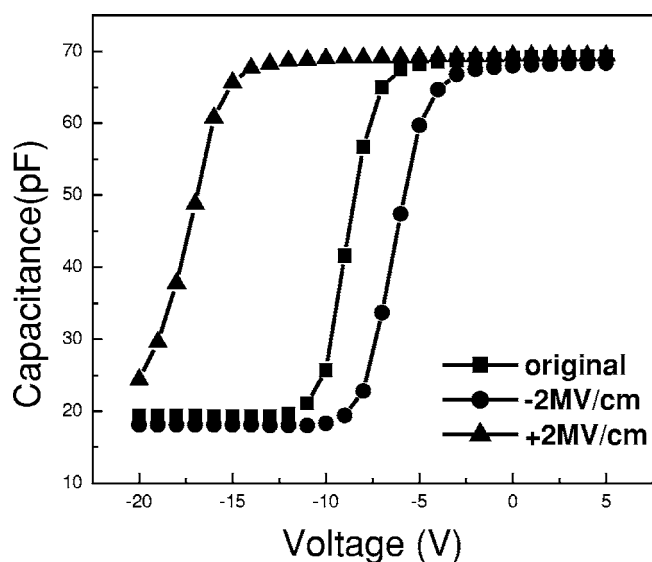


Figure 4. Capacitance-voltage curves of Al-MIS sample after electrical stress at 150°C -2 and +2 MV/cm for 4 min.

Table I. Flatband voltage shift of metal-MIS samples after bias temperature stress at 0.6 MV/cm for 30 min.

Temperature (°C)	Al-MIS (V)	Cu-MIS (V)	TaN-MIS (V)	Pt-MIS (V)
30	-7.48	-3.2	-2.74	-1.59
150	<-40	~-40	-9.6	-6.23

contaminated by mobile ions such as Na, K, Cu, etc.; (iii) the CDO film is polarized under electric field; (iv) charges are injected into the CDO film under electric field. In the following discussions, these mechanisms are examined one by one.

The quality of the 10-nm-thick thermal oxide was examined first. A simple Al/SiO₂ (10 nm)/Si MOS capacitor was fabricated. The dielectric constant obtained from high-frequency C - V measurement is around 4.0 with a flatband voltage of -0.2 V. No hysteretic phenomenon was observed during continuous C - V measurements. Therefore, the instability of the thin thermal oxide is ruled out.

Secondary-ion mass spectrometry (SIMS) analysis of blanket CDO film was performed to detect metal contamination. The mobile ions in CDO film, including Na, K, and Cu, are lower than the detection limit of SIMS analysis. But it had been reported that Al and Cu ions could be driven into CDO film during a BTS test. These metal ions could thermally diffuse along the nanoporous structures. The detailed mechanisms of metal ion drift and thermal diffusion in CDO film were discussed in our previous paper.²¹ The severe V_{FB} shift after BTS of these two kinds of samples can be attributed mainly to the metal ions. However, Pt as a noble metal and TaN being a diffusion barrier metal cannot be driven into CDO film, but the C - V instability phenomenon still occurs. This instability cannot be explained by mobile ions, and another mechanism must be considered. The dielectric polarization is thus examined.

It is known that the V_{FB} shift under continuous FVS and RVS may be attributed to dielectric polarization.²⁰ To avoid the influence of metal gate and metal deposition induced damage, the Al-MIS-2 structure with an additional 30-nm-thick PECVD SiO₂ between CDO and Al metal gate was used to study the role of dielectric polarization on the electrical instability. Silicon dioxide is known to be a good diffusion barrier of Al metal ions, and Al ions cannot drift across it.^{12,13,21} The stable C - V characteristics of reference sample Al/PECVD SiO₂/thermal SiO₂/Si structure indicate that both the PECVD SiO₂ film and the metallization process are well controlled.

Figure 5 shows the high-frequency C - V characteristics of Al-MIS-2 measured in both of the FVS and RVS modes for two cycles. The original curve was measured in the FVS mode with voltage

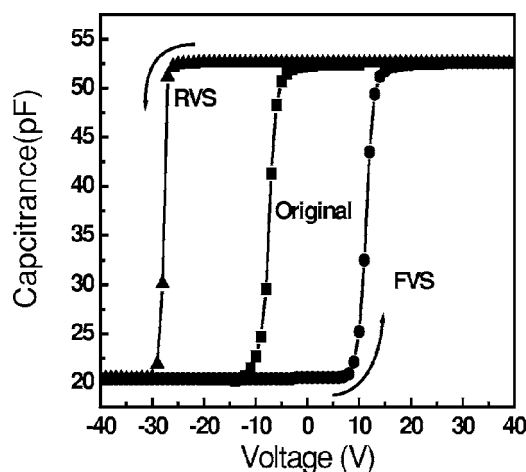


Figure 5. Capacitance-voltage curves of Al-MIS-2 sample with different voltage ranges and different sweep directions.

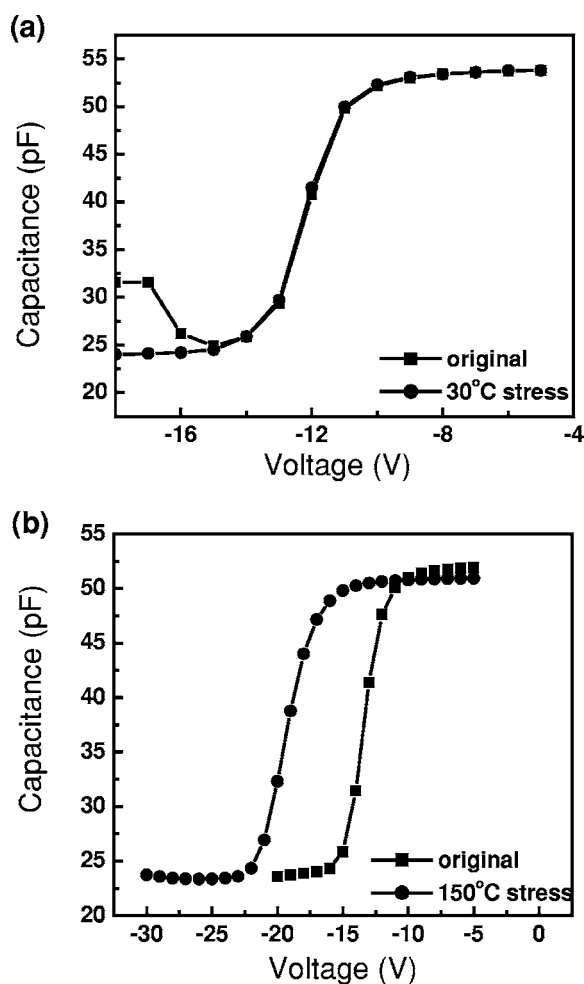


Figure 6. Capacitance-voltage curves result of Al-MIS-2 sample after BTS at (a) room temperature and (b) 150°C. The electric field is 0.6 MV/cm.

swept from -20 to $+10$ V. The original C - V curve looks like a normal C - V curve of a typical MIS capacitor. However, as the voltage range is expanded to ± 40 V, the C - V curve shifts apparently. In the FVS mode, the C - V curve shifted toward the positive voltage axis, while in the RVS mode, the C - V curve shifted toward the negative voltage axis. The magnitudes of V_{FB} shift in both directions are almost identical and the C - V curves are almost overlapped in continuous FVS and RVS measurement cycles. Because the electric field is only about 1.6 MV/cm (40 V/240 nm), the V_{FB} shift cannot be explained by electrons (or holes) injection from either gate or substrate through the SiO_2 layer. Therefore, the V_{FB} shift of the Al-MIS-2 sample could be attributed to dielectric polarization.²⁰

The Al-MIS-2 capacitor was electrically stressed at 0.6 MV/cm for 30 min. The V_{FB} shifts of the Al-MIS-2 sample stressed at 30 and 150°C are -0.07 and -5.12 V, respectively. The C - V curves are shown in Fig. 6a and b. The negligible V_{FB} shift of the Al-MIS-2 sample at 30°C indicates that the CDO film is electrically stable at room temperature. Figure 7 shows the Arrhenius plot of the magnitude of V_{FB} shift at 0.6 MV/cm. The extracted activation energy for dielectric polarization is 0.39 eV. It is observed that CDO film might cause V_{FB} shift more easily under higher-temperature stress condition. Besides, it is observed that the V_{FB} shift of TaN-MIS and Pt-MIS capacitors is slightly larger than the dielectric polarization induced V_{FB} shift, therefore an additional mechanism must be considered.

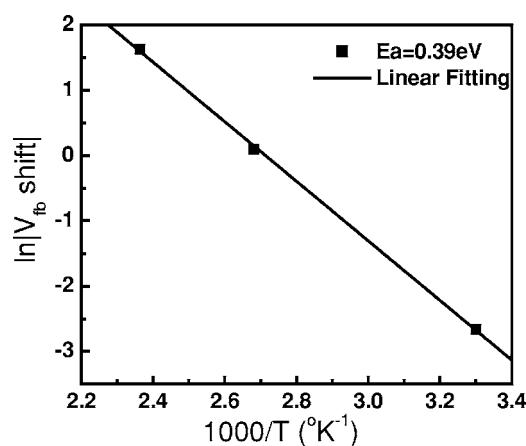


Figure 7. Arrhenius plot of the dielectric polarization of CDO film.

Carrier injection in CDO dielectric.—Although the dielectric polarization of CDO film can be used to explain the symmetric C - V shift under electric field and mobile ions can be used to explain the large V_{FB} shift under positive voltage stress with some kinds of metal electrode, there is still another possible mechanism that may cause V_{FB} shift, namely carrier injection and trapping in CDO film.

For metal-MIS samples biased at low electric field such as $+0.6$ MV/cm, it is hard for an electron to be injected from the Si substrate across thermal oxide into CDO film. Hole injection from the metal gate into CDO film is also unlikely. As metal-MIS samples are biased at -0.6 MV/cm, it is still hard for the hole to be injected from the Si substrate across thermal oxide into CDO film, but it is possible for an electron to be injected from the metal gate into CDO film. To study the carrier transport mechanism, the Al-MIS-3 sample with a nearly quasi-metal-insulator-metal (MIM) structure of Al/CDO/ N^+ -Si was fabricated. Figure 8a shows that the J - E characteristic at low temperature or low electric field can be well fitted with the Schottky emission (SE) model. At high temperature or high electric field, the J - E characteristic could be better fitted with the Frenkel-Poole (FP) model, as shown in Fig. 8b. The transition electric field from Schottky emission to Frenkel-Poole emission decreases with the increase of temperature.

Because FP emission is due to field-enhanced thermal excitation of trapped electrons into the conduction band, and the barrier height is the depth of the trap potential well, it is expected that FP emission can occur at lower electric field than Schottky emission. If the low field tunneling mechanism is Schottky emission, it is unreasonable for FP emission to dominate carrier transport at high field. Thus, the observation of Schottky emission at low electric field and FP emission at high temperature is unusual for dielectrics. To explain this phenomenon, the role of Al gate must be considered. It is postulated that the transition of the carrier transport mechanism might be attributed to the Al ions induced defects in bulk CDO. As has been reported in our previous paper, Al ions can be driven into CDO film by electric field.²¹ These Al ions produce trap sites there. More Al ions are driven into CDO film at higher temperature. Therefore, the trap site density increases with the increase of electric field and measurement temperature, and then the carrier transport mechanism changes from Schottky emission to FP emission at high electric field and the transition field decreases with the increase of temperature. This postulation is further verified by the measurement results of the Al-MIS-2 sample. Because of the capped thin PECVD SiO_2 layer on CDO film, Al ions cannot enter the bulk CDO. Figure 9 shows that the J - E characteristics of Al-MIS-2 at negative bias can be fitted with the Schottky emission model at high electric field even at 200°C.

Now the observed electrical instability can be understood with the model proposed in Fig. 10. Weak dielectric polarization occurs

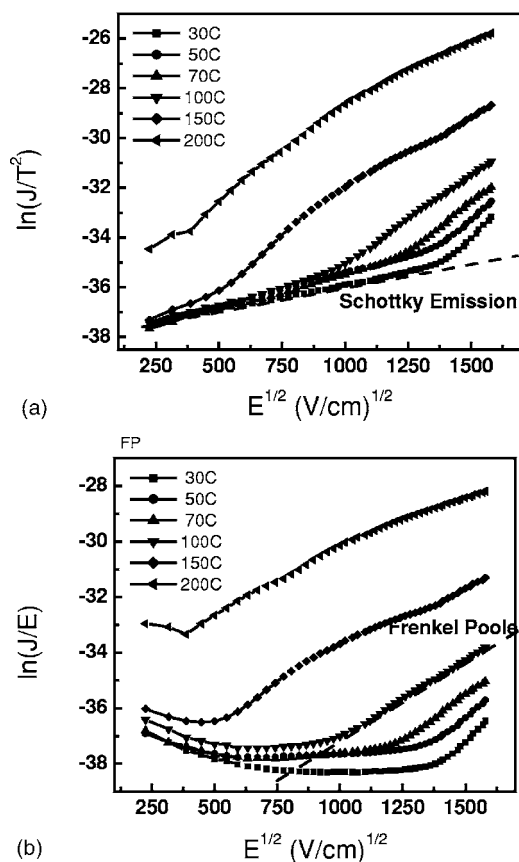


Figure 8. The J-E characteristic of Al-MIS sample can be well fitted by (a) the Schottky emission model at low temperature and low electric field, and (b) the Frenkel-Poole model at high temperature and high electric field.

under electric field at high temperature. If CDO film contacts with metal directly, electrons may be injected from the metal gate as the gate is negatively biased. Both dielectric polarization and electron injection cause slight V_{FB} shifts toward positive voltage direction. Because the leakage current of CDO film is very low, electron injection can be neglected at a typical operation condition of less than 0.2 MV/cm. As the gate is positively biased, metal ions such as Cu and Al would be driven into the porous CDO film. The positive

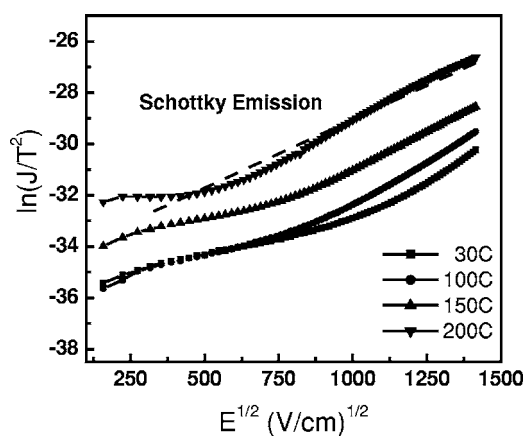


Figure 9. The J-E characteristic of Al-MIS-2 sample at negative gate voltage can be well fitted by the Schottky emission model from room temperature to 200°C.

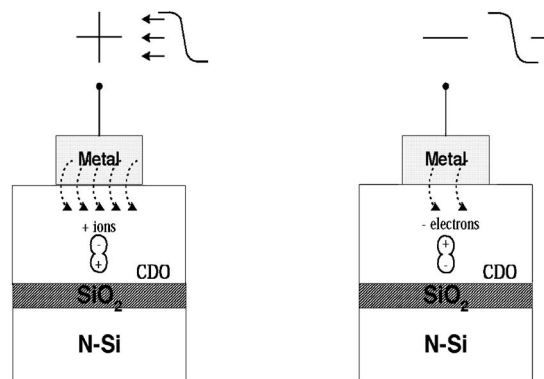


Figure 10. Proposed model to explain the observed electrical instability of metal-MIS capacitors.

metal ions result in a large V_{FB} shift toward the negative voltage direction. Combined with CDO dielectric polarization phenomenon, V_{FB} shifts dramatically.

Electrical reliability study of CDO film.—The time-dependent dielectric breakdown (TDDB) of Al-MIS, Cu-MIS, and TaN-MIS capacitors was evaluated at 1a, 1, and 3.5 MV/cm, respectively. Figure 11 shows the cumulative failure plot at a temperature of 200°C. It is observed that the lifetimes of the three kinds of samples are very close. Because the electric field of the TaN-MIS sample is much stronger than that of the other two samples, the lifetime of the TaN-MIS sample is much longer than that of the other two samples. It is known that no metal ions were driven into CDO films for the TaN-MIS sample. The long lifetime of the TaN-MIS sample reflects the actual reliability of the CDO film. As discussed in the preceding section, metal ions trapped in CDO film produce traps so that the carrier injection mechanism changes from Schottky emission to FP emission. It is also known that the TDDB lifetime is strongly related to defect density. The short lifetime of the Al-MIS sample and the Cu-MIS sample should be related to the injection of Al ions and Cu ions, respectively, into CDO film during the TDDB test.

It is known that the carrier transport mechanism at electric field lower than 10 MV/cm of the CDO film is Schottky emission but not FN emission and the CDO film is thick enough. It is supposed that the TDDB lifetime of the CDO film follows the E-model.²²⁻²⁴ Figure

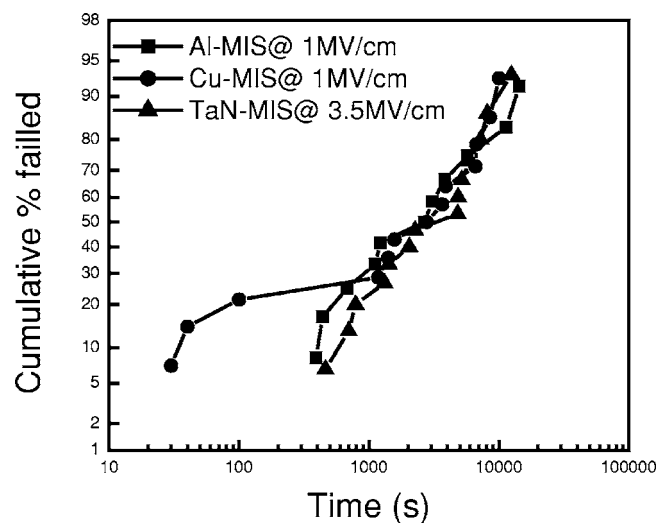


Figure 11. Cumulative TDDB failure of Al-MIS, Cu-MIS, and TaN-MIS samples stressed at 1, 1, and 3.5 MV/cm, respectively. The temperature is 200°C.

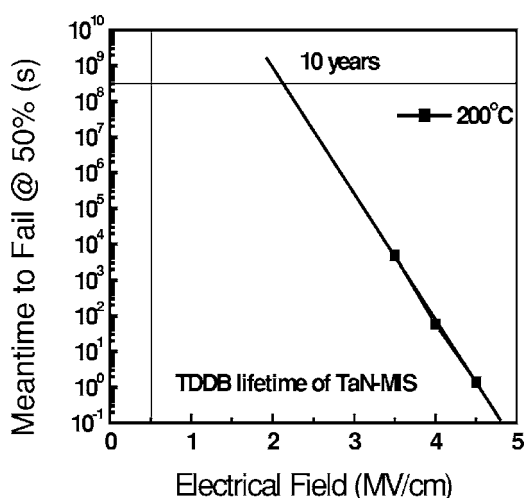


Figure 12. Extrapolation of TDDB lifetime of TaN-MIS sample at 200°C according to the E-model.

12 shows the mean time to failure (MTTF) of the TaN-MIS sample as a function of electric field at 200°C. The 10-year MTTF allows an electric field of stronger than 2 MV/cm, and the extrapolated MTTF at electric field of 0.5 MV/cm is much longer than 10 years by several orders of magnitude. These results indicate that the reliability of CDO film without metal contamination is well beyond the requirement of multilevel interconnection, and that TaN, the commonly used Cu diffusion barrier metal, is fully compatible with the CDO film.

Conclusions

In this work, the electrical instability of nanoporous carbon-doped oxide film was studied for the first time. Excellent basic properties including low dielectric constant (lower than 2.3) after annealing at 600°C, good thermal stability (no FTIR spectrum change after annealing at 650°C), very little thickness shrinkage (less than 3% after annealing at 650°C), and low leakage current (lower than 1 nA/cm² at 30°C and 2.5 MV/cm) are confirmed in this work.

However, in order to integrate CDO film into the complicated integrated circuits, the electrical stability and reliability must be evaluated carefully. In this work, an electrical instability model considering metal ion diffusion, dielectric polarization, and carrier injection was proposed to explain the observed electrical instability phenomenon of the CDO film under electrical stress. It is concluded that Al and Cu are not suitable metals to contact with CDO film directly because Al ions and Cu ions can be driven into CDO film easily. Fortunately, TaN, a barrier metal for the Cu-interconnect system, shows no mobile ion issues when in direct contact with CDO film. The electron transport mechanism is identified to be Schottky emission at low electric field and low temperature. As metal ions are injected into CDO film, for example Al and Cu, the electron transport mechanism changes to Frenkel-Pool emission at high temperature and high electric field. The injection of metal ions into CDO film also degrades the TDDB lifetime of the film. Fortunately, the

commonly used Cu diffusion barrier TaN is an excellent contact metal with CDO film. The 10-year TDDB lifetime allows an electric field stronger than 2 MV/cm and the TDDB lifetime at 0.5 MV/cm becomes longer than 10 years by several orders of magnitude. It is thus concluded that the nanoporous ultralow dielectric constant CDO film is a very promising intermetal dielectric material for next-generation interconnect systems.

Acknowledgments

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