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Copper Drift in Low-*K* Polymer Dielectrics for ULSI Metallization

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Abstract

This paper reports the drift of Cu ions in various low-permittivity polymer dielectrics to identify Cu barrier requirements for future ULSI integration. Bias-temperature stressing was conducted on Cu-insulator-semiconductor capacitors to investigate Cu^+ penetration into the polymers. Our study shows that Cu^+ ions drift readily into poly(arylene ether) and fluorinated polyimide, but much more slowly into benzocyclobutene. A thin nitride cap layer can prevent the penetration. A physical model has been developed to explain the kinetics of Cu^+ drift.

Introduction

Cu wiring has recently been demonstrated as a manufacturable multilevel metallization technology [1], [2]. This milestone has intensified the interest to integrate Cu with low-permittivity (low-*K*) polymer dielectrics [3]. The advantage of low-*K* polymers over conventional deposited SiO_2 (K = 4.0–4.5) in reducing parasitic capacitance allows interconnects to continue scaling with shrinking MOSFET gate dimensions while mitigating the severities of dynamic power dissipation, crosstalk noise, and signal propagation delays [4], [5].

With existing SiO_2 backend dielectrics, reliable integration requires Cu to be encapsulated with barrier materials since Cu^+ ions can rapidly drift through SiO_2 [6] to degrade field isolation, induce dielectric leakage [7], and even poison active devices [8]. However, the extent of Cu^+ penetration into low-*K* polymers, which directly impacts future Cu barrier requirements, has not been reported yet. In this paper, we evaluate the Cu drift behavior of three industrially relevant low-*K* polymers and propose a physical model to explain the kinetics of Cu^+ penetration.

Experimental

Cu- and Al-gate metal-insulator-semiconductor capacitors were fabricated with three low-*K* polymer dielectrics (Figs. 1 and 2): Schumacher PAE-2 poly(arylene ether) (PAE), DuPont FPI-136M fluorinated polyimide (FPI), and Dow Cyclotene™ 5021 benzocyclobutene (BCB). Following a 350°C forming gas anneal, the capacitors underwent bias-temperature stressing (BTS) in a N_2 ambient at 150–275°C with gate biases (V_{gate}) corresponding to electric fields of 0.1–1.0 MV/cm (Fig. 3). The N_2 ambient was essential to prevent Cu oxidation and moisture uptake in the polymer films (Fig. 4). The pre- and post-BTS capacitance-voltage (C–V) characteristics at 1 MHz were measured at 20°C without breaking the N_2 ambient. The gate current (I_{gate}) was monitored during BTS. I_{gate}–V_{gate} characteristics at various BTS temperatures were also obtained.

The low-*K* polymer films are sandwiched by thin oxide layers to prevent electron/hole injection from the gate into the polymers while allowing movement of Cu^+ under electrical bias, and to form a stable, high-quality interface with the Si substrate. Otherwise, charge instabilities associated with polymer/conductor interfaces complicate the C–V analysis [9]. Since Al does not drift into oxide [10], comparisons against the Al-gate controls have been drawn to differentiate between gate- and dielectric-related instabilities.

Results and Discussion

Fig. 5 shows examples of C–V results for capacitors subjected to BTS. The C–V behavior is unaffected by the thermal cycles if no bias is applied. For PAE and FPI capacitors, negligible flatband voltage shifts (ΔV_{FB}) are observed for negative V_{gate}. However, for positive

V_{gate}, ΔV_{FB}'s are much larger in Cu than in Al capacitors, demonstrating the penetration of Cu^+ ions into both PAE and FPI. The small shifts in Al capacitors, which eventually saturate with continued BTS, are attributed to trace alkali ions. Furthermore, the asymmetry of the *C–V* shifts with respect to bias polarity indicates that the applied bias during BTS was insufficient to induce bound polarization charge in the polymers [11]. For BCB capacitors, the *C–V* behavior is independent of gate metal. This indicates that the observed dielectric instabilities are not due to Cu^+ and that Cu^+ drift is significantly less in BCB than in PAE or FPI. To verify that Cu^+ is responsible for the large ΔV_{FB}'s in the PAE and FPI capacitors, BTS was performed on capacitors with PECVD nitride, a good Cu^+ barrier [7], replacing the deposited oxide cap as shown in Fig. 6. Indeed, the absence of *C–V* shifts confirms that Cu^+ penetration is prevented by the 750 Å nitride layer.

The measured ΔV_{FB}, I_{gate}–V_{gate}, and I_{gate}–*time* data (Figs. 5, 7, and 8 respectively) suggest that Cu^+ drift kinetics are governed by the physical model depicted in Fig. 9. A positive V_{gate} first ionizes Cu atoms and then injects the resulting Cu^+ into the oxide cap, giving rise to I_{gate}. Should Cu^+ ions penetrate readily into the polymer (PAE and FPI), they will accumulate at the polymer/thermal-oxide interface, establishing an uncompensated positive space charge near the Si substrate as evidenced by the negative shift in *C–V.* Field divergence from this space charge will lower the electric field at the gate interface and reduce the rate of Cu^+ injection (Fig. 7), consistent with the observed reduction of I_{gate} with time (Fig. 8). On the other hand, should Cu^+ be unable to penetrate into the polymer (BCB), the accumulation of Cu^+ space charge in the oxide cap will reduce the gate interface electric field to cease further injection of Cu^+. In this case, since the charge is located near the gate, the *C–V* behavior will be negligibly affected. Using I_{gate} as a quantitative measure of injected Cu^+, this model accurately predicts the measured ΔV_{FB} transients (Fig. 10). It is used to estimate the initial Cu^+ drift rates into the polymers (Fig. 11). The Cu^+ drift rate into PECVD oxynitride and deposited oxide are included for comparison [10].

Conclusions

Cu drifts readily into poly(arylene ether) and fluorinated polyimide, but much more slowly into benzocyclobutene. Cu integration with poly(arylene ether) and fluorinated polyimide will require dielectric or metal barrier encapsulation. Nitride or oxynitride liners are effective dielectric barriers provided they are sufficiently thin to preserve the low-*K* advantage of the polymer without compromising barrier integrity. Cu integration with benzocyclobutene will relax barrier requirements but is constrained by a reduced process temperature ceiling.

Acknowledgments

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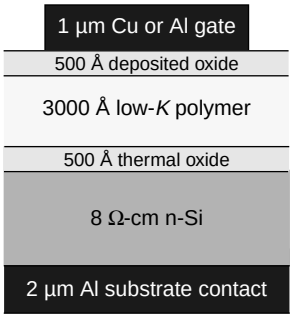

Polymers Investigated		*K*
PAE	poly(arylene ether)	2.8
FPI	fluorinated polyimide	2.6
BCB	benzocyclobutene	2.6

Fig. 1. Oxide-sandwiched low-*K* polymer dielectric capacitors for evaluation of Cu^+ drift. Gate area is 1 mm^2.

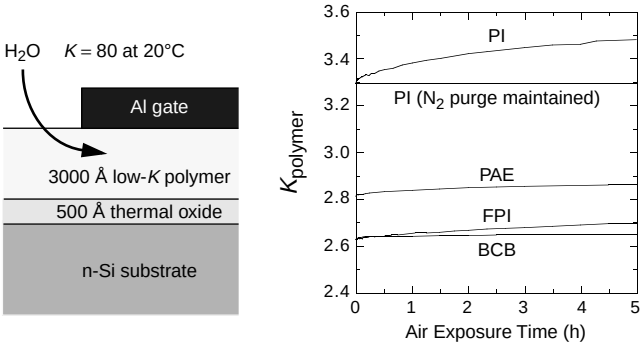

Fig. 4. Moisture uptake in low-*K* polymer after exposure to 40% RH air at 20°C. PI is abbreviated for DuPont PI-2556 polyimide.

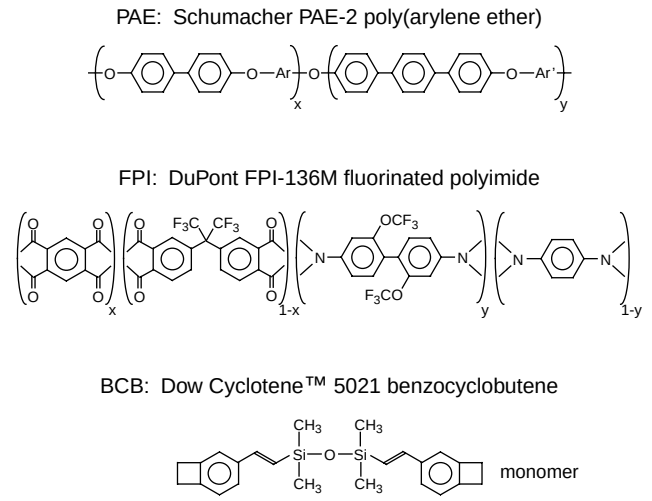

Fig. 2. Structural formulae of low-*K* polymer dielectrics.

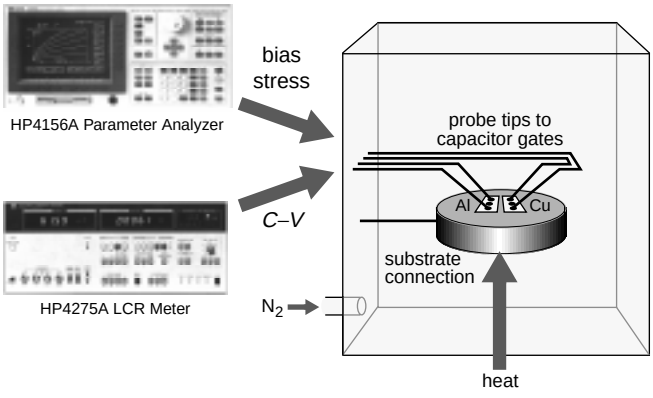

Fig. 3. Experimental setup for electrical testing. To prevent moisture uptake in the polymer, the pre- and post-BTS *C*–*V* measurements were conducted without breaking the N_2 ambient.

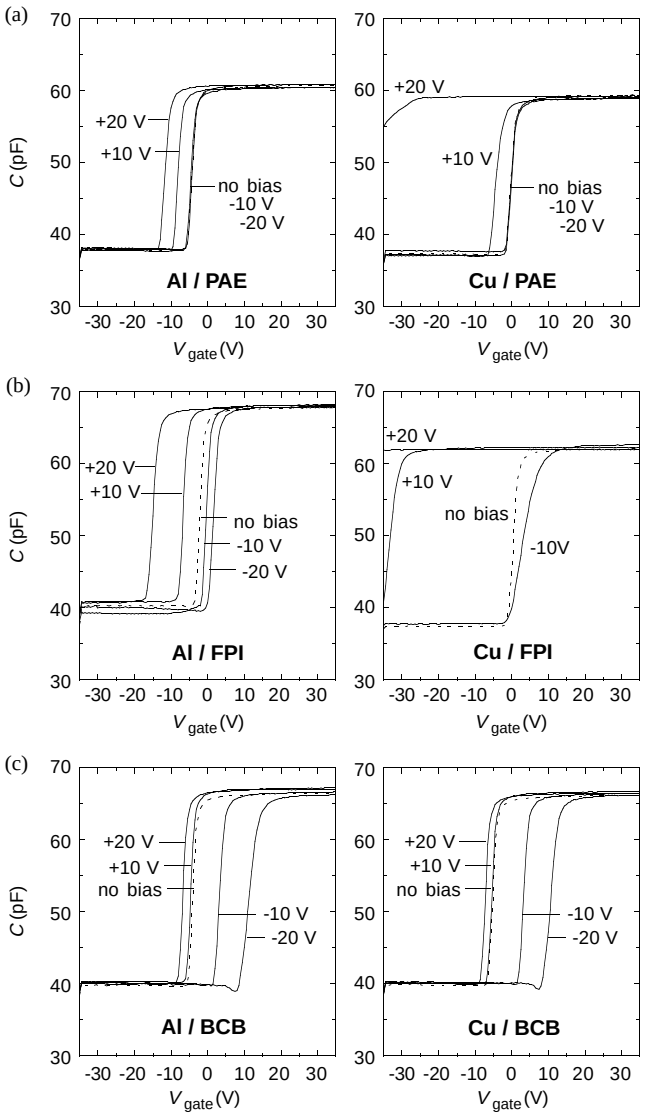

Fig. 5. *C*–*V* traces of oxide-sandwiched (a) PAE, (b) FPI, and (c) BCB capacitors stressed at 200°C for 1 h under various gate biases.

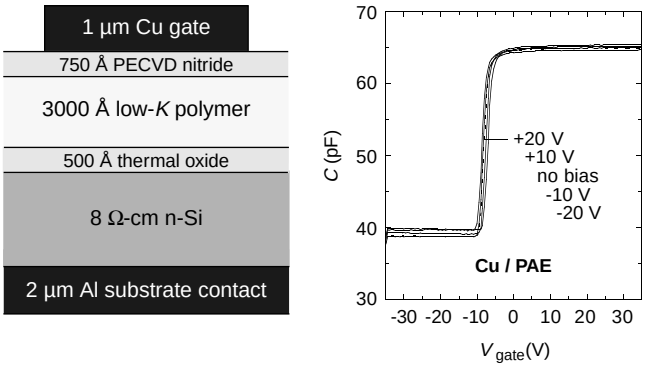

Fig. 6. *C*–*V* traces of nitride control capacitors stressed at 200°C for 1 h under various gate biases.

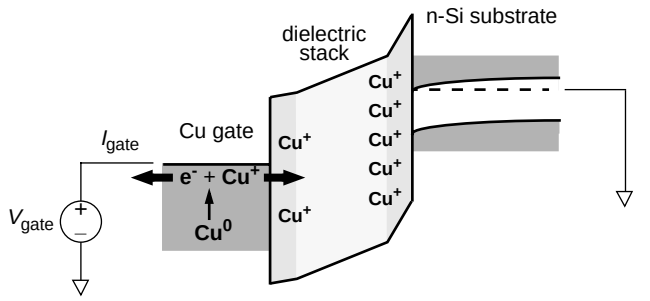

Fig. 9. Energy band diagram illustrating proposed kinetics of Cu^+ penetration. Cu atoms ionize, penetrate into the dielectric, and then accumulate in the dielectric as Cu^+ space charge.

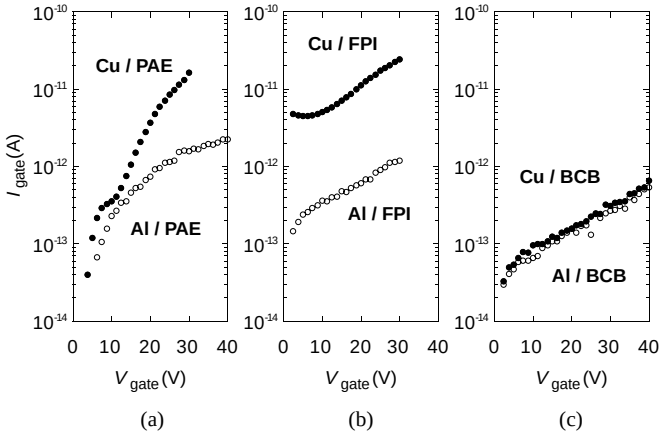

Fig. 7. I_{gate}–V_{gate} characteristics of oxide-sandwiched (a) PAE, (b) FPI, and (c) BCB capacitors at 200°C.

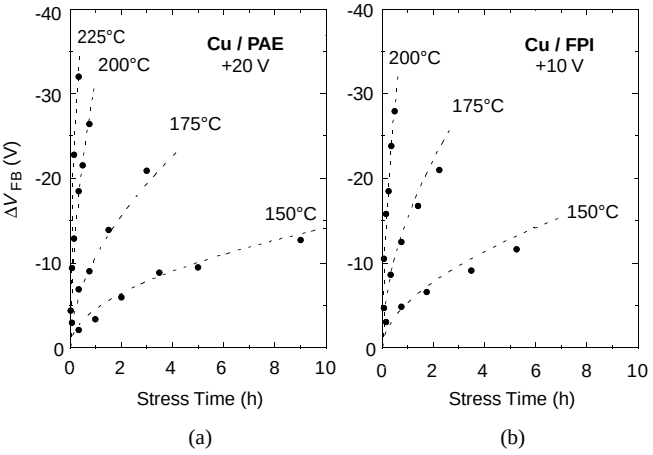

Fig. 10. Measured ΔV_{FB} transients (•) compared to model predictions (- - -) for Cu-gate (a) PAE and (b) FPI capacitors.

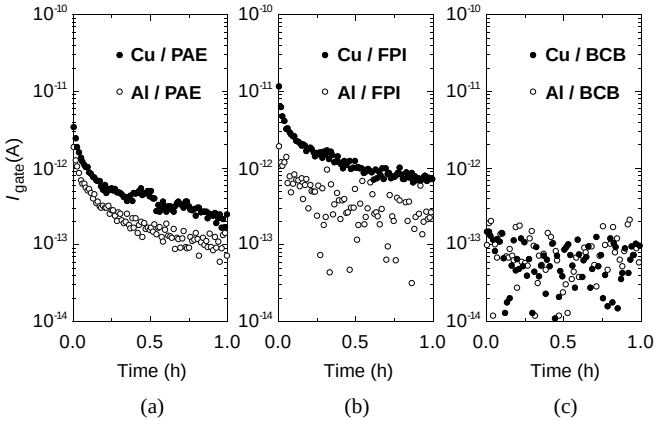

Fig. 8. I_{gate} transients during BTS of oxide-sandwiched (a) PAE, (b) FPI, and (c) BCB capacitors at 200°C under +20 V gate bias.

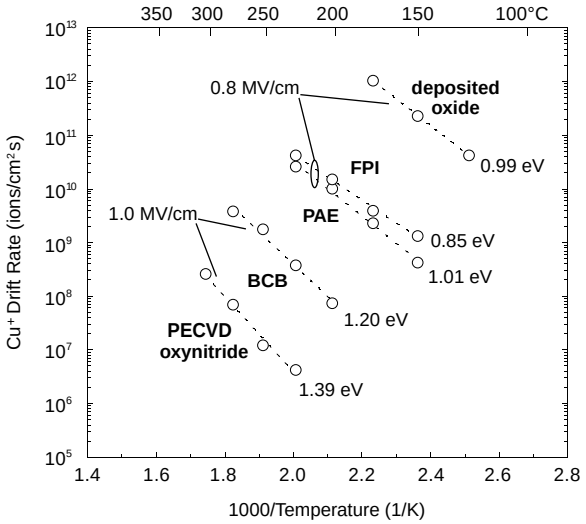

Fig. 11. Arrhenius plot of initial Cu^+ drift rates in various dielectrics.