

Kinetics of Copper Drift in PECVD Dielectrics

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Abstract— We quantified the drift of Cu ions into various PECVD dielectrics by measuring shifts in capacitance-voltage behavior after subjecting Cu-gate MOS capacitors to bias-temperature stress. At a field of 1.0 MV/cm and temperature of 100 °C, Cu ions drift readily into PECVD oxide with a projected accumulation of 2.7×10^{13} ions/cm² after 10 years. However, in PECVD oxynitride, the projected accumulation under the same conditions is only 2.3×10^{10} ions/cm². These findings demonstrate the necessity of integrating drift barriers, such as PECVD oxynitride layers, in Cu interconnection systems to ensure threshold stability of parasitic field n-MOS devices.

I. INTRODUCTION

COPPER (Cu) is a prime candidate as an alternative ULSI interconnection material since it offers both higher conductivity and better electromigration resistance over current aluminum (Al) alloys. However, many process integration issues exist, one of which is the rapid drift of positively charged Cu ions in SiO₂ under the influence of electric fields [1]. The presence of Cu ions in interlevel dielectrics (ILD's) may result in field threshold voltage instabilities, thus causing isolation problems.

Previous studies have detected Cu drift in thermal SiO₂ [2], [3] and in a variety of inorganic dielectrics [4] by capacitance-voltage (*C-V*) measurement of Cu-gate MOS capacitors subjected to bias-temperature stress (*BTS*). However, these studies did not quantify the magnitude of the reliability problem. In this study, we report the kinetics of Cu drift in PECVD oxide and oxynitride. *BTS* and *C-V* techniques were applied to determine flatband voltage shifts, ΔV_{FB} , versus stressing time at temperatures as low as 125 °C. While the presence of Cu atoms in the dielectrics is confirmed by secondary ion mass spectroscopy (SIMS), the *C-V* technique is primarily used to provide more sensitive determination of the Cu concentrations. We also discuss some dielectric charging effects.

II. EXPERIMENT

To conduct this study, 1 mm² Cu-gate MOS capacitors were fabricated on 7 Ω-cm n-type Si wafers. N-type substrates were selected so that the Si surface in the field region would

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be accumulated. First, 50-nm thermal SiO₂ was grown to form a good dielectric-to-substrate interface for well-behaved *C-V* characteristics. Next, a 150-nm PECVD dielectric, either oxide (SiO₂, $\epsilon_r = 4.1$) or oxynitride (SiO_xN_y, $\epsilon_r = 5.1$), was deposited at 300 °C. A 0.2-μm CVD Cu layer was subsequently deposited, patterned, and wet-etched to form the top gate electrode. Finally, 1-μm Al was sputtered on the wafer backside for a good substrate contact. For experimental controls, Al-gate capacitors on the same dielectric stack were also fabricated. Al does not drift in SiO₂ [5].

Prior to *BTS*, the capacitors were annealed at 300 °C in nitrogen for 80 min. *C-V* characteristics of unannealed capacitors exhibited V_{FB} variations and *C-V* spreadout, indicating interface charges and traps which were likely introduced by plasma exposure during dielectric deposition. The pre-*BTS* anneal was sufficient to ensure that all capacitors exhibit similar *C-V* characteristics before the stress testing.

Both Cu and Al capacitors were subjected to *BTS* with constant DC gate voltages, V_G , corresponding to initial electric fields, E_O , of -1.0, 0, and +1.0 MV/cm at temperatures ranging from 125 °C to 300 °C. High-frequency (1 MHz) *C-V* characteristics were obtained before and after stressing to evaluate ΔV_{FB} . All *BTS* runs were conducted in a nitrogen-purged box to prevent Cu oxidation. Samples were heated to the test temperature and bias was subsequently applied for durations ranging from a few minutes to a few days depending on the test temperature. Finally, with the bias removed, the capacitors were quenched down to 50 °C within 1 min to prevent backdrift of ions.

III. RESULTS AND DISCUSSION

The *BTS* results for PECVD oxide are examined first. After the pre-*BTS* anneal, the flatband voltages for Cu and Al capacitors were 0.24 ± 0.06 V and -0.52 ± 0.03 V respectively. The difference in the flatband voltages reflects the difference in the metal work functions. Capacitors were stressed in the 125 °C to 200 °C range. For all tested conditions, unbiased Cu and Al capacitors exhibited a negligible V_{FB} shift less than 0.03 V. With a positive field of $E_O = +1.0$ MV/cm ($V_G = +20$ V), we observed significant negative ΔV_{FB} and no *C-V* spreadout in Cu capacitors, indicating the introduction of primarily positive bulk charge, as opposed to interface traps, into the dielectric [Fig. 1(a)]. In contrast, the *C-V* characteristics of corresponding Al capacitors did not change after *BTS*. Hence, the positive charge in the Cu capacitors could not be bias-induced positive charge in the dielectrics or at the interfaces [6], but must be Cu ions.

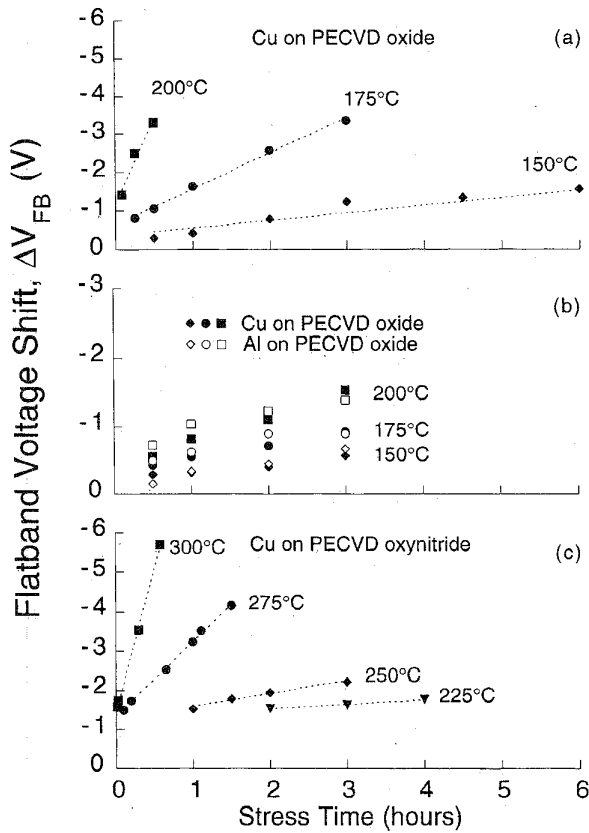


Fig. 1. ΔV_{FB} as a function of stress time and temperature for (a) PECVD oxide capacitors at $E_O = +1.0$ MV/cm, (b) PECVD oxide capacitors at $E_O = -1.0$ MV/cm, and (c) PECVD oxynitride capacitors at $E_O = +1.0$ MV/cm.

With a reversed field of $E_O = -1.0$ MV/cm ($V_G = -20$ V), we observed slightly negative ΔV_{FB} from both Cu and Al capacitors although we expected slightly positive or no ΔV_{FB} [Fig. 1(b)]. These positive bulk charges are believed to originate from hydrogen-related instabilities present in deposited oxides [7], [8]. However, since ΔV_{FB} 's were similar for both Cu and Al capacitors, this phenomenon could not be attributed to Cu.

Similar results were obtained for PECVD oxynitride capacitors [Fig. 1(c)]. Since Cu drift was significantly slower in PECVD oxynitride than in PECVD oxide, the stress temperatures ranged from 225 °C to 300 °C for comparable ΔV_{FB} .

As a confirmation of Cu in the dielectric, SIMS analysis was performed on two Cu capacitors—one with oxide and the other with oxynitride—stressed at +1.0 MV/cm and 250 °C for 1 h (Fig. 2). Consistent with the observed ΔV_{FB} 's, the SIMS profiles show a large quantity of Cu reaching the oxide-substrate interface in the case of oxide, with very little Cu in the case of oxynitride.

The drift rates of Cu ions, $d[Cu^+]/dt$, were extracted from the slopes of the best-fit lines in Fig. 1. We ignore large $|\Delta V_{FB}|$ data since the presence of a significant amount of Cu ions in the dielectric would change the electric fields in the dielectric during stressing. Also, by using the slopes, we

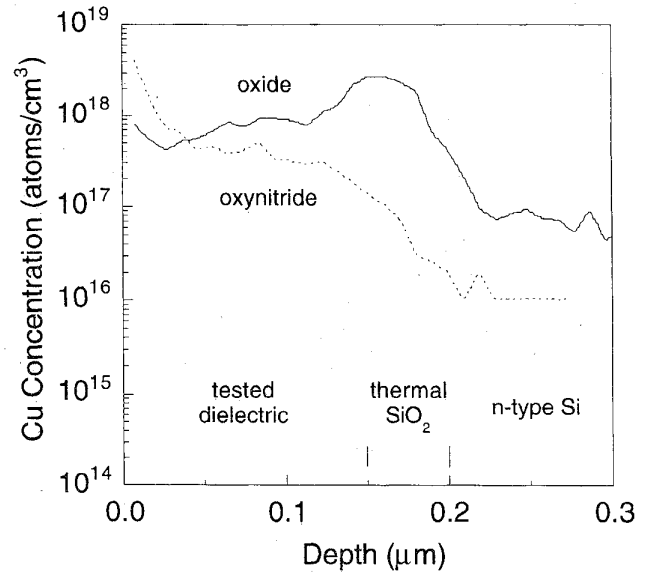


Fig. 2. SIMS analysis of Cu capacitors with oxide and oxynitride dielectrics. Capacitors were stressed at +1.0 MV/cm and 250 °C for 1 h. The Cu gates were stripped by wet-etching prior to analysis.

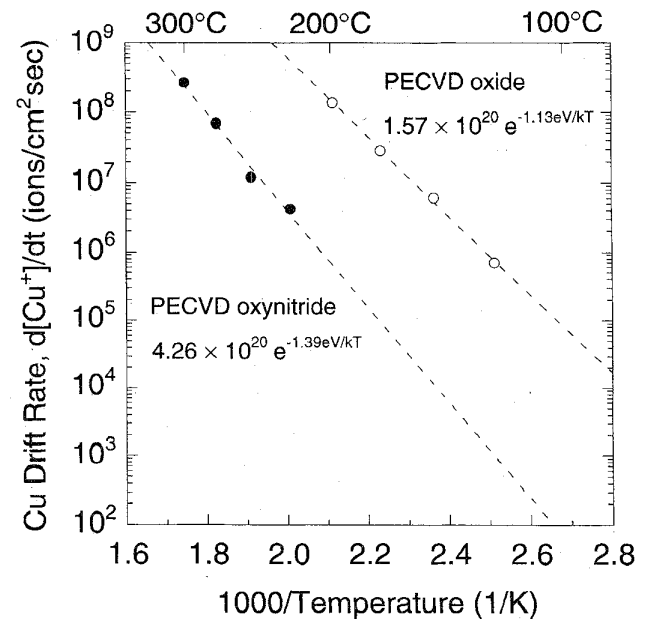


Fig. 3. Arrhenius plot of Cu drift rates in PECVD oxide and oxynitride.

segregate the effect of any trace alkali contaminants (Na^+) which we believe are responsible for the initial rapid change in V_{FB} . The effect of these faster moving alkali ions saturates when the limited ions accumulate at the oxide-substrate interface, leaving subsequent increases in ΔV_{FB} to be due to the slower Cu ions. For example, in the case of PECVD oxynitride [Fig. 1(c)], the best-fit lines clearly extrapolate back to a common ΔV_{FB} -intercept of about 1.3 V.

ΔV_{FB} was converted to $[Cu^+]$ by assuming that the Cu ions had drifted to the oxide-substrate interface in order to

obtain a lower-bound estimate

$$\frac{d}{dt}[Cu^+] = -\frac{C_{OX}}{q} \frac{d}{dt}(\Delta V_{FB}) \quad (1)$$

where C_{OX} is the dielectric stack capacitance per unit area and q is the electronic charge. The calculated rates are summarized in Fig. 3 where activation energies of 1.13 eV and 1.36 eV were extracted for PECVD oxide and oxynitride respectively. The amount of Cu^+ accumulation after 10 years operation at a nominal chip temperature of 100 °C and a bias of 1.0 MV/cm was extrapolated. Under these conditions, the projected $[Cu^+]$ in PECVD oxide and oxynitride are 2.7×10^{13} and 2.3×10^{10} ions/cm² respectively. For a 0.5 μ m PECVD oxide ILD, the calculated $[Cu^+]$ would correspond to a threshold instability of -600 V. However, the instability would be reduced by three orders of magnitude for the case of PECVD oxynitride. A previous study has shown that PECVD nitride is even more resistant to Cu drift than PECVD oxynitride [4]. Unfortunately, the higher dielectric constant of PECVD nitride will render it unacceptable for interconnect applications.

IV. CONCLUSIONS

We have determined the drift rates of Cu ions in PECVD oxide and oxynitride using bias-temperature stress and capacitance-voltage techniques. Cu ion movement in PECVD oxide could pose a very serious instability concern if Cu interconnects are to be integrated without drift barriers.

PECVD oxynitride is a candidate material exhibiting both a good barrier property and backend process compatibility.

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