Accelerated Debonding and Cracking in Thin-Film Structures: Chemical Reaction Rate and Loading Effects

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ABSTRACT

Considerable research efforts are being directed at exploiting organosilicate and organic nanoporous thin-films and integrating these materials into next generation devices such as biosensors, size-selective membranes, microfluidic structures, photovoltaic cells, and microelectronics. While these films possess some very attractive properties, the Si-O-Si backbone of nanoporous glasses renders the matrix mechanically fragile and susceptible to stress corrosion cracking in moist environments. Organic layers exhibit significant local plasticity and may be susceptible to fatigue processes. Moreover, fabricating, packaging, and operating high performance devices typically involves exposure to harsh aqueous solutions which may significantly accelerate crack growth rates and lead to premature device failure.

Recent studies by our group have revealed that debonding of interfaces with nanoporous glass layers in microelectronic interconnect structures, and cracking in the layers themselves, are greatly accelerated in the presence of chemical species typically encountered during processing such as chemical mechanical planarization (CMP). In organic or metal layers, more complex thermomechanical or vibrational loading may even result in classic fatigue processes. Such accelerated cracking involves the synergistic effect of fragile dielectric glasses, chemical species from the environment, and residual and applied thin film stresses. In addition, complex interactions of the environment with the layers themselves lead to unexpected changes in the crack driving force through significant changes in the surface energy of the materials. The focus of our research has been to characterize and model these complex processes in order to understand adhesion and accelerated cracking in thin-film structures for future generation devices. Here we demonstrate the significant effect of CMP solution chemistry on interfacial adhesion and crack growth rates in nanoporous LKD thin-films as well as lithographically patterned structures containing copper and LKDs. A new mechanism of accelerated cracking in H_2O_2 environments is revealed.

INTRODUCTION

The success of next generation interconnect devices relies to a large extent on the design and fabrication of structures containing LKDs that are capable of surviving CMP processing. Integrating LKDs into multilevel interconnects has, however, been limited due to their extremely brittle nature and susceptibility to stress corrosion cracking in chemically active environments. Stress corrosion cracking is a time-dependent mode of failure that occurs at loads well below those required for critical or catastrophic fracture [1,2]. Despite the intense interest in these materials, there is currently a paucity of experimental data and little understanding regarding how aqueous solution chemistry influences crack growth. Indeed, often times CMP slurries are formulated to optimize polishing rates and minimize dishing while little consideration is given to the effect these environments have on reducing adhesion and accelerating crack growth. Understanding how solution chemistry may accelerate cracking and thus device reliability is essential for nanoporous LKDs to be viable candidates for interconnects.

The synergistic effect of moisture and mechanical loads is known to greatly accelerate crack propagation rates in SiO_2 thin-films [3,4]. Recently, the effect of hydrogen peroxide was also demonstrated to have a significant effect on the rate of cracking in LKD thin-films [5], however, the effect of the additional chemical species present in CMP slurries has yet to be determined. In addition, virtually nothing is known about the effect these solutions have on crack growth in lithographically patterned structures containing LKDs and copper. Accordingly, the objective of this research was to characterize and model subcritical

crack growth in a new commercially available nanoporous methylsilsesquioxane (MSSQ) blanket thin-films as well as patterned structures tested in simulated CMP environments.

Significant effects of the CMP slurry chemistry were observed on crack propagation rates. In general, high pH solutions were observed to accelerate growth rates, while low pH solutions inhibited cracking of the dielectric. Anomalously high growth rates were observed in weakly acidic hydrogen peroxide solutions commonly used in copper CMP slurries. The mechanisms of crack growth are elucidated and modeled in terms of mass transport of active chemical species and stress enhanced chemical reaction rates. Ultimately, our objective is to understand the effects of CMP environment on the mechanical reliability of fragile nanoporous LKD thin-film glasses and provide general guidelines for the formulation of CMP slurries that minimize cracking of interconnect structures.

EXPERIMENTAL

Double cantilever beam (DCB) sample geometries were fabricated by sandwiching MSSQ thin-films (JSR 6103 and JSR 5109) between two elastic silicon substrates. The dielectric constant of the 6103 and 5109 MSSQ were 1.9 and 2.2. The films were nominally 400 nm thick and contained pores of ~1.5 nm in diameter. Two technologically relevant cap layers were utilized to determine the effect on interfacial adhesion: SiC and a highly cross-linked, ductile aromatic polymer (Figure 1). Arrays of patterned lines of copper and the JSR 5109 MSSQ were fabricated using lithographic techniques. The structures selected for study had line widths of 500 nm and were 300 nm in height. The copper lines were encased with a ~10 nm layer of TiN barrier a schematic cross section is shown in Figure 1.
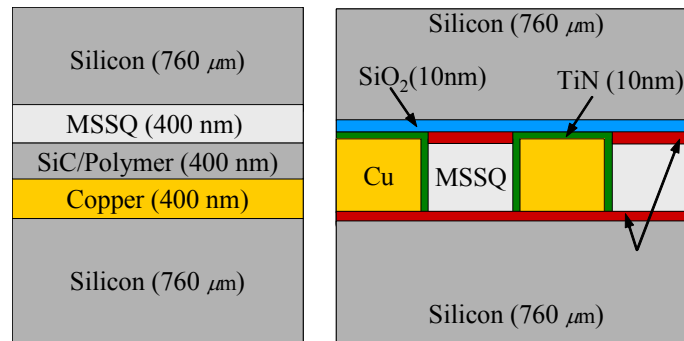

Figure 1. Blanket and patterned thin-film structures employed to examine effect of CMP slurry chemistry on adhesion and the rate of crack growth.

Subcritical crack growth rates, da/dt, were characterized as a function of the applied strain energy release rate, G (J/m^2), over the range of 10^{-4} m/s to ~10^{-10} m/s using load relaxation fracture mechanics techniques [3,4]. This method involves loading the specimen at a constant displacement rate to a predetermined load then fixing the displacement. The ensuing time-dependent load relaxation resulting from crack growth increases the specimen compliance from which the crack length, a, da/dt, and G may be determined.

Testing was conducted in an aqueous environmental chamber with controlled temperatures. A range of salient solution chemistries were employed to examine the effects on crack growth rates. These included buffered acidic and basic solutions of pH 3 and 11, water (pH6), 3wt% hydrogen peroxide solution (pH5) and 3wt% hydrogen peroxide solution with sodium hydroxide (pH12). After testing, the fractured specimens were carefully examined using high resolution characterization techniques to determine the debond path.

RESULTS and DISCUSSION

Subcritical crack growth rate as a function of G, observed for water, the buffered solutions, and the 3% hydrogen peroxide are shown in Figure 2 for the 6103 MSSQ with polymeric cap [5]. The accelerating effect

of the basic solutions and the inhibiting effect of the acidic solutions is readily apparent. For example, at a given value of G (which might correspond to a particular residual stress in the structure), growth rates are increased by almost one order of magnitude in the basic solution compared to the water, where as growth rates were decreased in the acidic solution by a similar amount.
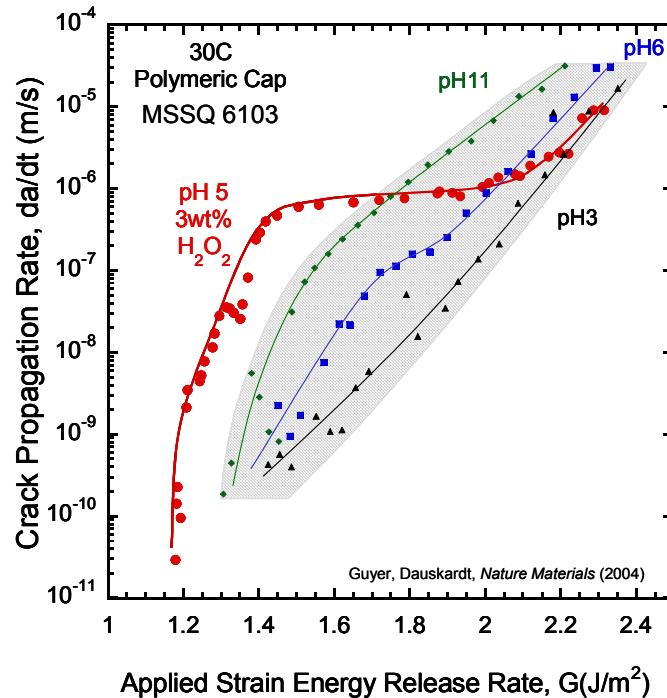

Figure 2. Subcritical crack growth behavior showing the significant effect of buffered solution pH on cracking in porous MSSQ with polymer cap. XPS fracture path analysis revealed cohesive failure of the MSSQ.

In addition, subcritical crack growth thresholds, G_{th}, representing values of G below which crack growth is essentially dormant were decreased from ~ 1.4 J/m^2 (pH 3) to ~ 1.3 J/m^2 (pH 11). Technologically, values of G below G_{th} represent a safe processing region, and thus it is of extreme importance to understand how solution chemistry affects this portion of the curve. The observed crack growth behavior can be rationalized in terms of a stress-enhanced chemical reaction that occurs at the crack tip similar to the reaction that occurs in bulk glasses [1,2], however, the transport of species to the crack tip may also act as a rate limiting step for the reaction. The increase in growth rates and decrease in G_{th} with pH is attributed to the nucleophilic attack of strained Si – O crack tip bonds by hydroxide ions in solution.

Copper CMP slurries often contain hydrogen peroxide as an oxidizer and the effect of this molecule on cracking rates is clearly evident in Figure 1. At high values of G (>2.2 J/m^2), a reaction controlled region was observed which is consistent with that expected for an equivalent pH solution. On the other hand, at low values of G (<1.4 J/m^2), a new reaction controlled region was apparent with anomalously high crack-growth rates, significantly exceeding those reported for even the strongly basic solution. At intermediate values of G a classic transport limited regime was observed and was attributed to the transport of H_2O_2 molecules to the crack tip. The enhanced reaction kinetics in the presence of H_2O_2 is attributed to the extremely unstable O–O bond which cleaves when the molecule interacts with the crack tip bonds, forming two highly reactive hydroxide radicals [5].

Similar effects were observed for the 5109 MSSQ with SiC cap in H_2O_2, however, steric hindrance of the molecules was observed near 0.9 J/m^2 [5], as shown in Figure 3.
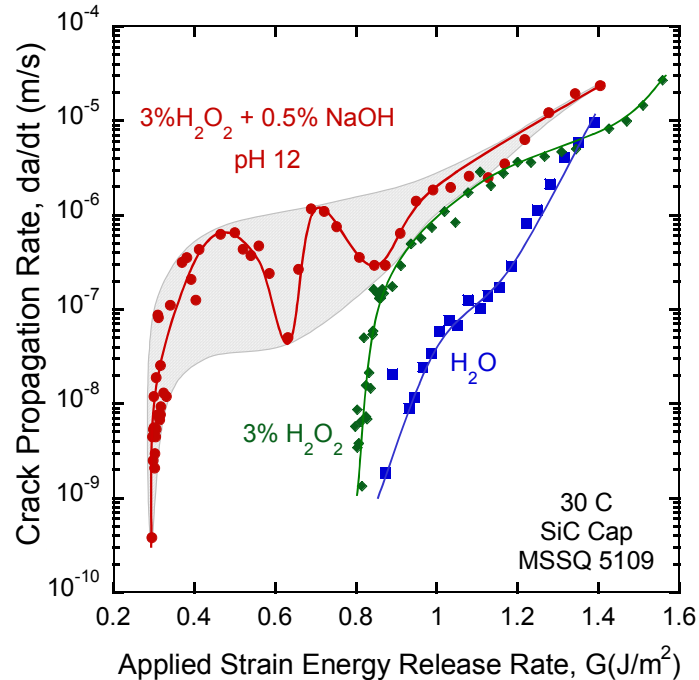
Figure 3. The corrosion of MSSQ in H_2O_2 + NaOH solutions allows cracking to extend to extremely low values of G.

An interesting and important effect is realized when sodium hydroxide is added to the H_2O_2 solution (Figure 3). The crack growth behavior at high values of G is consistent with that of a basic environment, as again, the H_2O_2 molecules will be transport limited from reaching the crack tip. With decreasing G, cracking behavior resembles that of the 3% H_2O_2 solution, however, near 0.9 J/m^2 a marked acceleration is observed. This phenomenon is due to the general corrosion of the MSSQ crack flanks. In other words, when the molecules begin to be come sterically hindered from reaching the crack tip and growth rates decrease, the corrosion of the surface allows the H_2O_2 molecules to reach the crack tip, accelerating crack growth. The molecules again become sterically hindered, which decreases growth rates until the corrosion again allows the molecules to reach the crack tip. This continues until the reaction threshold for the Si – O crack tip bonds and H_2O_2. This greatly decreases G_{th} from 0.8 to 0.3 J/m^2 resulting in significant cracking acceleration.

Cracking in the lithographically patterned structures subjected to the pH 3 and 11 buffered solutions as well as water and 3% H_2O_2 is consistent with that observed in the blanket thin-films when growth is parallel to the features (Figure 4). The accelerating effect of basic solutions and inhibiting effect of acidic solutions is clearly apparent. The decrease in G_{th} (1.4 J/m^2 at pH 3 to 0.7 J/m^2 at pH 11) is of great technological importance as this results in a 4 order of magnitude change in crack velocity. The anomalous effect of the weakly acidic H_2O_2 is evident and also represents a significant decrease in G_{th} as well as growth rate acceleration.

Crack growth orthogonal to the features differs significantly from that in the parallel orientation and the mechanisms responsible for this will be discussed in the presentation. In addition, other salient CMP as well as lithographic solution chemistries will be considered along with design strategies including energy dissipation by plastic deformation.
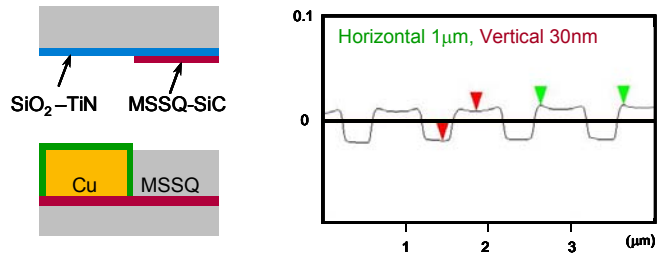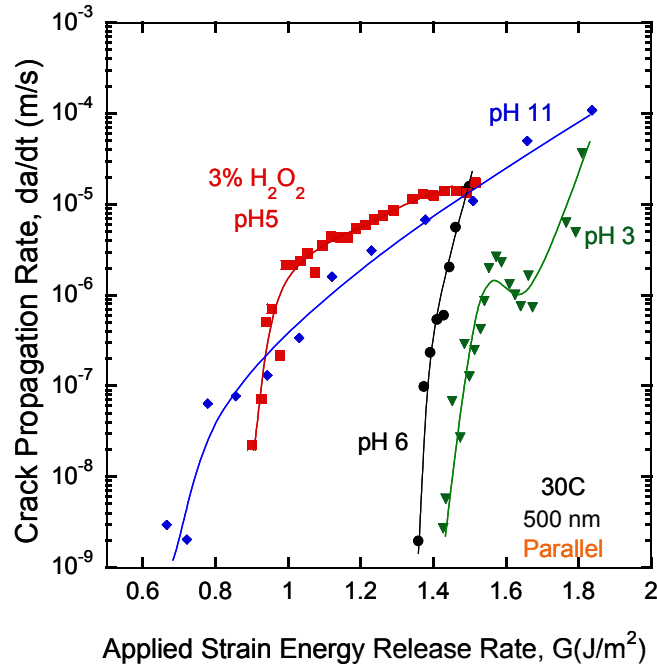
Figure 4. Effect of aqueous solution pH on subcritical crack growth for 500nm width lines and cracking parallel to the features. Fracture path analysis reveals debonding at the $TiN-SiO_2$ and MSSQ-SiC interfaces.

CONCLUSIONS

This research demonstrates the important effect of CMP solution chemistry on the rate of chemically assisted crack growth in MSSQ blanket thin-films as well as lithographically patterned structures containing copper and MSSQ. In general, crack growth rates were enhanced by basic solutions and inhibited by acidic solutions. Anomalous cracking behavior was observed in weakly acidic hydrogen peroxide solutions, as growth rates exceeded even of basic solutions, particularly at reduced driving energies. The implications of these findings are extremely important as planarizing electroplated copper in multilevel metallization schemes typically requires CMP slurry formulations containing hydrogen peroxide.

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