LETTER

Selective Deposition of a Cross-Linked Low-Permittivity Polycarbosilane on Copper

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ABSTRACT Differential scanning calorimetry studies of the reaction of a cyclolinear polycarbosilane [cyclo-$(CH_3Si(CH_2)_2SiCH_3)$-$(CH_2)_6]_n$ on air-exposed Cu surfaces reveal a substantial enhancement of the cross-linking rate compared to noncatalytic surfaces, e.g., Au, Ag, Al, Si. The increased rate is attributed to surface Cu(II)-catalyzed opening of the embedded disilacyclobutane rings in the polymer. This rate enhancement is used to selectively deposit a cross-linked polycarbosilane on copper patterns in exclusion to the silicon substrate surface. These results could be attractive for realizing metal-dielectric interfaces for applications in nanodevice wiring and packaging.

KEYWORDS: polycarbosilane • catalytic ring-opening • copper surface • selective cross-linking.

INTRODUCTION

Integrating low dielectric permittivity (low *k*) insulators with metals is a critical issue for diverse applications, e.g., nanodevice wiring in integrated circuits (1), laminates for high-frequency electronics (2), communications and packaging (3), and coatings and composites (4). This is particularly problematic for metals such as Cu, where adhesion to most ceramic or organic coating materials is weak. Moreover, the generation and transport of Cu ions along the interface and/or into the coating (5) often compromise interface functionality. Conventional solutions of using intermediary layers of refractory metals or their compounds are effective for many applications, but may be inapplicable for emerging technologies (5). For example, realizing an adherent Cu—low *k* dielectric interface (6) while inhibiting interfacial mixing remains a challenge for nanodevice wiring. Even though nonporous low *k* polymers with inhibited copper uptake (7) have been obtained, intermediary layers are required to overcome poor bonding between metals and low polarity moieties characteristic of low *k* polymers. Using separate barrier/glue interfacial layers (8) greater than 5 nm thick is not an option for devices with nanoscale features (9) (e.g., <30 nm), necessitating completely new approaches to directly integrate polymers with metals. Recent works showing that molecular nanolayers with apposite terminal moieties can immobilize copper and enhance adhesion through strong interfacial bonding (10), offering promise for obviating separate intermediary layers altogether, for example, by incorporating metal-binding chemical moieties into polymeric precursors of low *k* materials (11).

Here, we demonstrate the direct integration of a low *k* polymer with copper without interlayers by means of catalyzed cross-linking at the metal—polymer interface. We show that catalytic ring-opening in a cyclolinear polycarbosilane triggered at the interface results in accelerated cross-linking, leading to the selective thermosetting of a polymer film on copper lines patterned on a Si wafer. This result, in the context of recent work (12) showing that the same polycarbosilane can be rendered strongly adherent to copper without separate intermediary layers and with only a modest permittivity increase (e.g., from $k \approx 2.4$ to ≈ 2.7), holds promise for realizing low *k* polymer—metal interfaces for many emerging applications such as nanodevice wiring and packaging.

We have previously reported the preparation (13) and electrical properties (7) of cross-linked carbosilane films with $k = 2.4$ by curing a spin-coated cyclolinear polycarbosilane [*cyclo*-$(CH_3Si(CH_2)_2SiCH_3)$-$(CH_2)_6]_n$, CLPCS that contains strained disilacyclobutane (DSCB) rings in the polymer main chain (see Figure 1a). Differential scanning calorimetry (DSC) studies of this CLPCS in standard Al pans show a well-defined exotherm at ca. 280 °C corresponding to irreversible polymer cross-linking via DSCB ring-opening indicated by solid-state NMR and infrared spectroscopy (13).

In the present study, we carried out DSC studies of the polymer in Cu-coated pans and determined the relative rates of cross-linking of this polymer on Cu and on a noncatalytic Al surface using Kissinger analysis (14) of the exothermic peak temperatures as a function of the heating rate. The results of these studies and experiments on a Cu-patterned Si wafer show that CLPCS cross-linking is substantially accelerated on copper, due to the presence of a surface Cu_xO layer formed due to air exposure. Although copper-containing compounds and copper nanoparticles are known to

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Received for review May 19, 2010 and accepted July 23, 2010
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DOI: 10.1021/am100441t
2010 American Chemical Society

Published on Web 08/09/2010

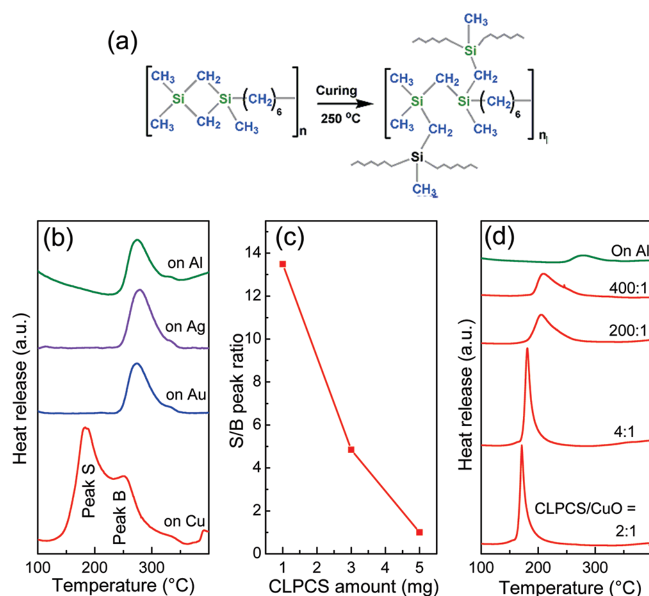

FIGURE 1. Structure and ring-opening behavior of CLPCS-(CH_3Si-$(CH_2)_2SiCH_3$)-$(CH_2)_6]_n$ on different air-exposed metal surfaces. (a) Schematic sketch showing DSCB ring-opening and cross-linking in CLPCS. (b) DSC exotherms obtained at 10 °C/min from CLPCS on Cu or Al, Ag, and Au. S and B peaks correspond to surface-triggered and bulk reactions, respectively. (c) S/B peak ratios for different CLPCS amounts on Cu. (d) DSC scans from mixtures of CLPCS and CuO powder [Cu(II)] with different CLPCS/CuO mole fractions. A reference scan from Al is also shown for comparison.

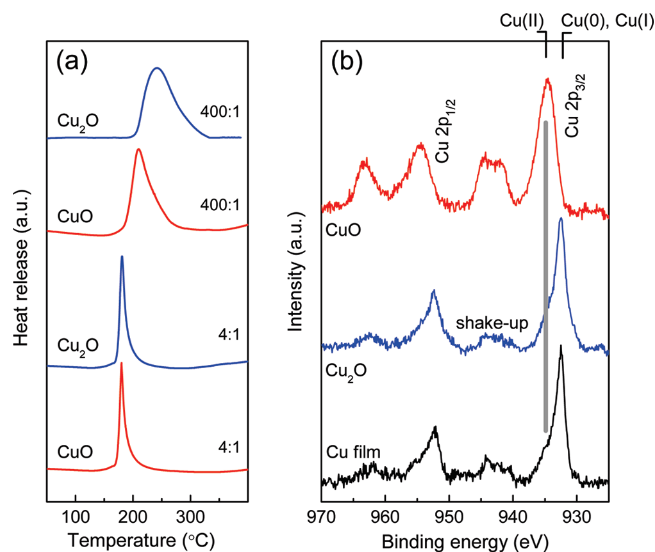

FIGURE 2. (a) DSC scans from CLPCS-Cu_xO [x =1 ≡ Cu(II); x = 2 ≡ Cu(I)] mixtures for CLPCS/Cu_xO = 4 and 400. (b) XPS spectra from Cu_2O and CuO particles. The shoulder at ~934 eV (gray vertical line) and the 940−945 shakeup indicate Cu(II), whereas the sub-band near ~932 eV corresponds to Cu(0) and/or Cu(I) states.

catalyze DSCB ring-opening (15−17), the use of such a catalytic reaction to selectively deposit films of a cross-linked insulating polymer on a Cu-patterns on a Si substrate demonstrated here is new and could be adapted for device fabrication and processing.

RESULTS AND DISCUSSION

Figure 1b shows DSC scans obtained at 10 °C/min for the CLPCS in Al DSC pans coated with Cu, Ag and Au. Heating the CLPCS in Cu-coated DSC pans reveals exotherms that are substantially different from that associated with DSCB ring-opening and the cross-linking of the polycarbosilane (13) in uncoated Al pans. In contrast to the solitary exothermic peak observed for uncoated Al pans, we observe two exothermic peaks at ~180 and ~250 °C for Cu-coated DSC pans. The lower temperature peak labeled "S", absent in DSC scans of CLPCS on Al, is attributed to CLPCS cross-linking induced on the copper surface. We label the higher temperature peak, which is close to the solitary peak observed for Al, as "B" to denote bulk cross-linking (13) of the CLPCS. Our peak assignments are corroborated by the S/B area ratio increase seen when the surface-cross-linking fraction is increased by decreasing the CLPCS amount on Cu (Figure 1c), e.g., a 5-fold decrease in CLPCS fraction increases the S/B area ratio by a factor of 14.

DSC scans of mixtures of CLPCS and Cu_xO [x = 1 for Cu(II); x = 2 for Cu(I)] powders comprising ~5 μm particles carried out to amplify the surface reaction while mimicking the air-exposed Cu surface (Figure 1d) suggest that the Cu(II) state catalyzes ring-opening. Solitary exothermic peaks observed in the 180−210 °C range in experiments with CuO powders are in the same range as the S peak seen for CLPCS on air-exposed Cu film surfaces in the Cu-coated pans. Increasing the particle fraction (and hence the surface area) by decreasing the CLPCS/CuO molar ratio from 400:1 to 2:1 lowers the S peak maximum by 40 °C, indicative of Cu(II) catalyzed ring-opening on CuO surfaces. Mixtures of CLPCS and Cu_2O exhibit S peaks at higher temperatures (see Figure 2a), indicating that Cu(I) oxide is less active than Cu(II). For example, at low Cu_xO powder fractions (CLPCS/Cu_xO=400:1), the S peak is ca. 30 °C higher for Cu_2O than for CuO.

At high Cu_xO powder fractions (e.g., CLPCS/Cu_xO = 4:1), the ring-opening temperatures are almost identical for both oxides, pointing to similarities in surface chemistry on both oxides. This is confirmed by the presence of Cu(II) on Cu_2O particle surfaces, indicated by the core-level shoulder at ~934 eV and the shakeup sub-band (see Figure 2b). These results and the fact that air-exposed Cu films exhibit a Cu(II) signature indicate that accelerated cross-linking on air-exposed Cu films is due to the presence of a Cu_xO surface layer that is comprised, at least in part, of Cu(II). This conclusion is supported by our prior studies (12) showing that electron transfer to surface Cu(II) is concomitant with DSCB ring-opening that occurs by surface-bound oxygen attacking the Si in DSCB rings to form $-CH_2$ radicals that propagate polymer cross-linking through successive inter-chain DSCB ring-opening steps.

Kinetics studies carried out by Kissinger analysis of the S and B peak temperatures as a function of the heating rate for the CLPCS in Cu-coated DSC pans confirm that the copper surface-catalyzed ring-opening rate is significantly higher than the rate of ring-opening in the bulk. Decreasing the heating rate shifts the S and B peaks to lower temperatures (see Figure 3a) and increases the S/B area ratio, as expected for increased surface cross-linking. Additionally, CLPCS surface cross-linking on Cu commences ca. 70 °C lower than the onset of cross-linking on Al, suggesting a

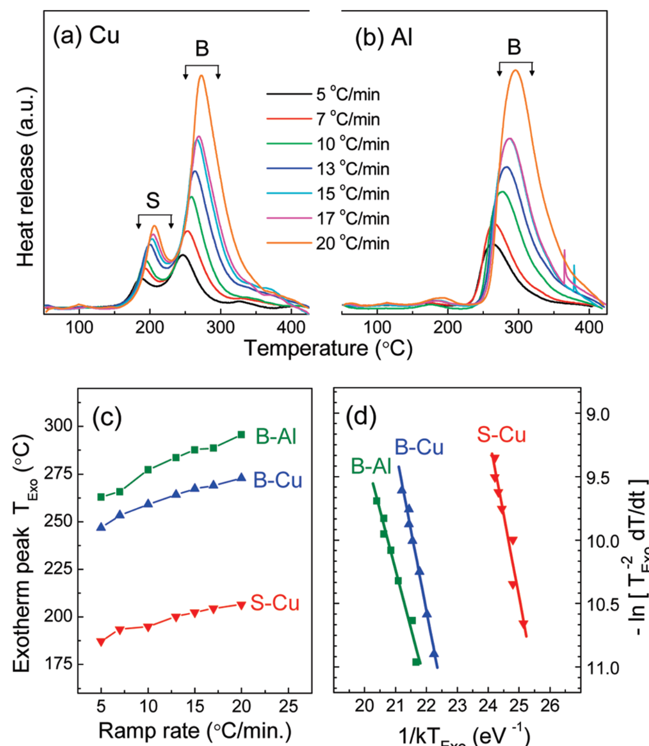

FIGURE 3. Kinetics analysis of ring-opening on Cu and Al surfaces. DSC scans for CLPCS on (a) Cu and (b) Al. (c) Exotherm peak temperature maxima T_{Exo} for CLPCS for different ramp rates. (d) Kissinger plots obtained from the analysis of T_{Exo} for polymer cross-linking on Al and Cu. S and B denote surface and bulk cross-linking, respectively.

Table 1. Kinetics Parameters for CLPCS Cross-Linking on Air-Exposed Al and Cu[a]

metal	surface		bulk	
	E_S (eV)	P_S (s^{-1})	E_B (eV)	P_B (s^{-1})
Al			0.93 ± 0.1	2.7×10^8
Cu	1.3 ± 0.1	6.13×10^{13}	1.3 ± 0.1	2.0×10^{11}

[a] $r_i = P_i \exp(-E_i/kT)$, where $r_i \equiv$ reaction rate coefficient, $E_i \equiv$ activation energy, i = S ⟹ surface, i = B ⟹ bulk, $k \equiv$ Boltzmann constant, $T \equiv$ absolute temperature.

catalytic reaction on the air-exposed copper surface (see Figure 3b,c). Kissinger analysis (14, 18) of the S and B peak temperatures T_{Exo} measured at different heating rates yields an activation energy $E_{BAl} = 0.93 \pm 0.1$ eV (19) for bulk cross-linking on Al, which is lower than $E_{SCu} = E_{BCu} = 1.3 \pm 0.1$ eV obtained for surface-induced and bulk cross-linking on copper (see Figure 3d and Table 1). The higher E_{SCu} is, however, offset by the pre-exponential factor P_{SCu} for the surface reaction being more than a hundred-thousand-fold greater than P_{BAl} for cross-linking on Al, and several hundred-fold higher than P_{BCu} for bulk cross-linking on Cu. The higher P_{SCu} than P_{BCu} is consistent with the higher probability of catalytic opening of the rings proximal to the copper film surface. As a result, the surface cross-linking rate coefficient r_{SCu} is greater than that for bulk cross-linking on both Cu and Al surfaces (r_{BCu} and r_{BAl}, respectively; see Figure 4a), confirming the catalytic effect of the Cu surface.

Our analysis showing $P_{BCu} > P_{BAl}$ suggests that the surface-catalyzed ring-opening on copper accelerates bulk ring-opening as well. Estimates of the spatial extent of CLPCS cross-linking induced by surface-catalyzed and bulk ring-opening from enthalpy values extracted from the respective DSC peak areas corroborate this observation. In particular, the surface-catalyzed cross-linking enthalpy increases with increasing CLPCS amount and saturates at $\Delta H_{SCu} \approx 0.5$ J for 9 g of CLPCS, when the corresponding bulk cross-linking enthalpy $\Delta H_{BCu} \approx 1.7$ J (see Figure 4b). Assuming a polycarbosilane density of 0.93 g/cm^3 (13) and a planar reaction front on a copper pan surface area of ~15 mm^2, the saturation enthalpy for the surface reaction corresponds to a ~150 μm thick polycarbosilane film, confirming that surface-catalyzed ring-opening influences cross-linking far beyond the metal–polymer interface. Furthermore, the identical E_{SCu} and E_{BCu} values for copper (see Table 1) point to closely coupled mechanisms for surface-catalyzed and bulk cross-linking, e.g., bulk cross-linking occurs by a radical chain process triggered by catalyzed ring-opening at the copper-polymer interface.

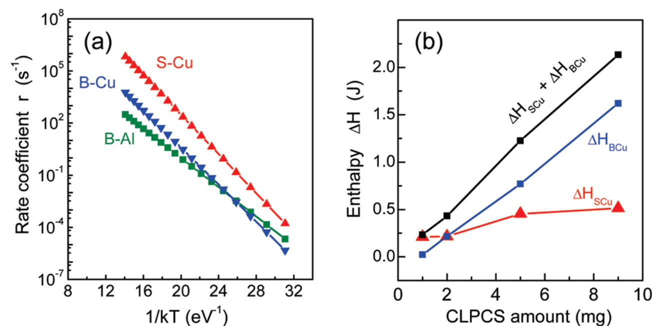

FIGURE 4. Rate coefficients and enthalpies of ring-opening on Al and Cu. (a) Reaction rate coefficients for bulk and surface cross-linking processes for CLPCS on Al and Cu obtained by Kissinger analysis. (b) Enthalpies for surface-reaction and bulk cross-linking of CLPCS on Cu extracted by DSC analysis plotted as a function of CLPCS amount.

Surface-catalyzed ring-opening gives rise to a combination of two important features that provide a unique basis for directly integrating Cu with CLPCS-derived dielectrics. First, the influence of surface-catalyzed ring-opening on bulk cross-linking is a valuable attribute for scalable fabrication and decreasing thermal budgets for integrating low k polymers on metals. Second, surface-catalyzed cross-linking can be harnessed for selective formation of a thermoset dielectric on Cu, e.g., in exclusion to silica. For instance, we observe a 3-fold higher CLPCS cross-linking rate (ratio of CLPCS thickness on Cu than that on silica at $t_{curing} \sim 8$ min, see Figure 5) and a smaller incubation time for the onset of cross-linking on copper compared to that on silica when a film of the CLPCS is heated at 160 °C on a Cu-patterned Si wafer surface (see Figure 5a). Infrared spectra (Figure 5b) show the exclusive presence of a completely cross-linked polycarbosilane film (13) on Cu upon curing for $t_{Curing} < 4$ min, whereas cross-linking does not commence on silica for the same curing time. Furthermore, the thermoset polycarbosilane films show $k \approx 2.4$, which (12, 7) surpasses the currently projected requirement for nanodevice wiring (20). Selective copper-catalyzed cross-linking could be exploited for integrating carbosilane interlayer dielectrics on Cu wiring,

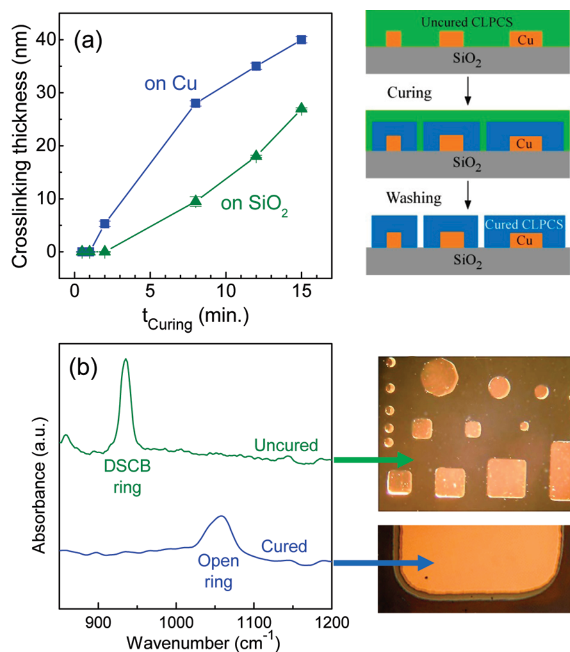

FIGURE 5. Selective CLPCS ring-opening and cross-linking on copper. (a) Cross-linked polycarbosilane film thickness on copper, and on silica, as a function of curing time t_{Curing}. CLPCS thickness was measured by variable takeoff angle XPS for thicknesses below 5 nm, and spectroscopic ellipsometry for higher thicknesses. (b) Infrared spectra demonstrating selective CLPCS cross-linking on Cu at 165 °C for 4 min; no cross-linking is detectable on silica for this t_{Curing}. The schematic sketch on the right captures the processing sequence carried out to demonstrate selective cross-linking. Representative optical micrographs and regions from which the infrared spectra were obtained are also shown.

or for facilitating self-aligned device processing (21) by using the polycarbosilane as etch- or planarization-stop layers.

CONCLUSIONS

In summary, we have shown that copper catalyzes the cross-linking of a cyclolinear polycarbosilane with embedded disilacyclobutane rings, leading to the formation of a thermoset film with $k \approx 2.4$. Surface-catalyzed ring-opening triggers accelerated bulk cross-linking at lower temperatures, providing a means to selectively thermoset the polymer on copper in exclusion to noncatalytic surfaces such as silica and Al. These results, combined with the impermeability of polycarbosilanes to copper intake (7), their excellent thermal stability—up to 400 °C for short periods and 350 °C for hours (13)—the high Cu/carbosilane interface fracture toughness (12), along with the relatively low dielectric constant, open up new possibilities for integrating carbosilane-based dielectrics for applications in nanodevice processing, wiring, packaging, high-frequency electronics, coatings, and composites.

EXPERIMENTAL DETAILS

We prepared a [cyclo-$(CH_3Si(CH_2)_2SiCH_3)$-$(CH_2)_6]_n$, with $n \approx 10\ 000$ by addition/metathesis polymerization of a bis-butadiene-substituted disilacyclobutane catalyzed by a ruthenium catalyst, followed by hydrogenation of the internal double bonds (13). Residual ruthenium was removed by filtration through a silica column and reprecipitation with methanol. DSC measurements of CLPCS were carried out in an inert helium environment with Al pans purchased from TA Instruments, and pans coated with ∼1 μm thick Cu in a CVC DC magnetron tool at 7 mTorr Ar, followed by air annealing at 150 °C for 2 h to oxidize the Cu surface. In one set of experiments, different amounts of CLPCS ranging from 0.5—5 mg were heated from 100 to 450 °C at a constant rate of 10 °C/min. In the second set, 5 mg CLPCS samples were heated at different ramp rates between 5—20 °C/min. We also conducted CLPCS curing experiments in pans coated with Au or Ag using e-beam deposition.

Cu patterns ranging from 1 × 1 mm^2 to 6 × 6 mm^2 were created on precleaned Si wafers by sputter-depositing Cu through a shadow mask with mm-scale features. A 420 ± 10 nm thick CLPCS film was then spin-coated from a 15% solution in xylene at 3000 rpm for 30 s, and annealed at 165 °C in flowing N_2 for different times to induce surface-catalyzed cross-linking. Film thickness was measured using spectroscopic ellipsometry and variable takeoff angle XPS for less than 5 nm film. Uncured CLPCS was removed by washing with xylene and samples were dried in flowing nitrogen. Surface chemistry was studied by XPS using a PHI 5400 instrument with a Mg K_α beam. The adventitious C1s peak at 285 eV was used as internal calibration to correct for spectral shifts induced by charging. Infrared spectra were acquired using a Nicolet Magna IR 560 spectrometer.

Acknowledgment. This work was supported by the New York State Foundation for Science, Technology and Innovation (NYSTAR) through the TTIP program and a grant from the NSF through DMR 0519081.

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