Calorimetry of Polymer Metallization: Copper, Calcium, and Chromium on PMDA-ODA Polyimide

Richard Murdey and J. Todd Stuckless

Contribution from the Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1

Received October 5, 2002; E-mail: johntodd@chem.ubc.ca

Abstract: The heat of reaction has been measured for vapor deposition of metal atoms onto clean polymeric substrates. These calorimetric measurements introduce a new technique for the study of metal−polymer interfacial chemistry. Results for three systems are reported here, calcium, chromium, and copper on PMDA-ODA polyimide, and widely different reaction heats are observed in each case. Our results show that calcium deposition is very exothermic at low coverages, with an initial heat approaching 610 kJ/mol. In the case of chromium deposition, the initial heat is quite low, 125 kJ/mol or less, an affect we attribute to the energetic cost of polymer bond disruption. The data for copper deposition show that calorimetry can be used to study fine details of the nucleation and growth process of the metal island film.

Introduction

The chemical properties of metal−polymer interfaces can be crucial to the performance of microelectronic devices which incorporate polymers as semiconducting films or insulating layers. Specific attributes of interest include thermal stability, adhesion strength, and charge injection barriers. With the development of novel organic based devices, it becomes critical to better understand the chemistry of the metallized polymer interfacial region, systems which can be very difficult to study spectroscopically.

The polymer substrate used in this study, pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimide, is a low dielectric insulator with good thermal and chemical stability. It has been used commercially as a high-performance interconnect material, motivating many published studies of its metallization, particularly with copper and chromium.[1] Most of these studies rely on spectroscopic probes, especially using XPS to determine the effective oxidation state of the interfacial polymer and metal atoms. We feel that calorimetric measurement of the heat evolved during metallization, which depends directly on the energy of the chemical bonds formed or broken during the formation of the interface, can provide fundamentally important new data. Knowledge of the metal binding energies will aid substantially in performing quantum chemical calculations and in modeling the kinetics of diffusion and growth processes.

Experimental Section

Ultrahigh vacuum adsorption calorimetry is a technique developed by Prof. King's group[2,3] and extended to metallization studies by Prof. Campbell's group.[4] Our apparatus is the first designed for polymer metallization experiments; details of its design and construction will be published at a later date. In the experiment, metal atoms are vapor deposited onto a thin polymer film which is coated onto a pyroelectric sensor. This sensor is a lithium tantalate crystal with gold plated surfaces. Each pulse of atoms from the chopped effusive metal source generates a voltage signal upon deposition, which is calibrated by comparison to the signal due to heating with a known laser input. The differential molar heat of reaction is proportional to the voltage peak height divided by the number of metal atoms delivered during the pulse.

Pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimide films were formed directly on the sensor face by ex-situ spin-coating of a solution of polyamic acid in *N*-methyl pyrrolidone (NMP) and subsequent curing to 700 K under vacuum. The thickness of the PMDA-ODA film was about 1 μm. The samples were either used shortly after being cured or degassed at 500 K for several hours prior to the measurements. The ultrahigh vacuum chamber allowed in-situ sample transfer from the curing/degassing stage to the gated metallization/calorimetry stage. The operating pressure during metal deposition was on the 10^{-9} Torr scale, with samples exposed for several hours in total to this background gas, composed mainly of hydrogen and carbon monoxide outgassing from around the oven. While these sample conditions are fairly typical of UHV polymer metallization studies found in the literature, possible effects due to sample impurity should be kept in mind. As an indication, however, that adsorption of background gases is not significant, the reaction heats are unchanged before and after interrupting each metal deposition for a time similar to the metallization period.

The metal atom source was a high-temperature evaporation cell. Alumina crucibles were used in all cases. The flux at the sample was 25 atoms/nm^2·min for copper, 9 atoms/nm^2·min for Ca, and 4 atoms/nm^2·min for Cr. After a collimating aperture, the thermal atom beam passes through a rotating chopper followed by a velocity selector. The slots on the two velocity-selector chopper wheels are staggered to block any line-of-sight radiation between the hot oven and the detector. At the selectors highest rotation speed, a significant fraction of the metal

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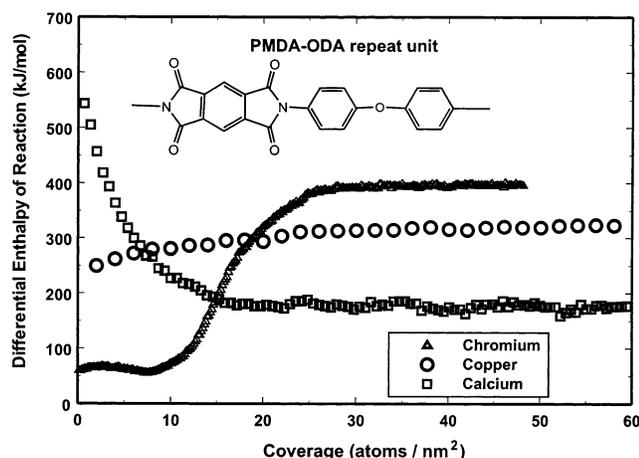(4) Stuckless, J.; Frei, N. A.; Campbell, C. T. *Rev. Sci. Instrum.* **1998**, *69*, 2427.

Figure 1. Differential enthalpy of reaction for copper, chromium, and calcium deposited on a PMDA-ODA polyimide film as a function of metal coverage.
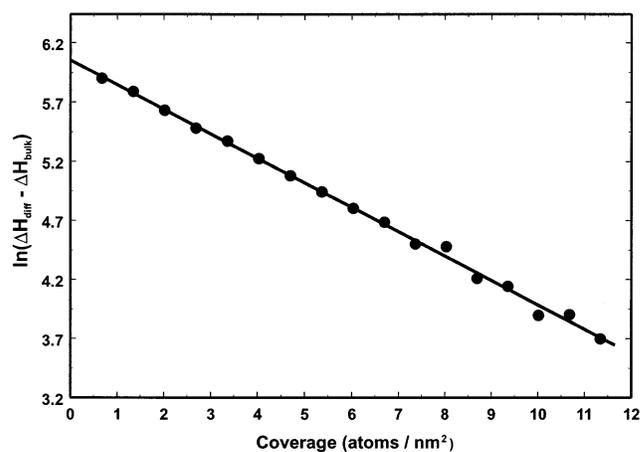

Figure 2. Calcium data of Figure 1 replotted to show that the decay of the differential enthalpy toward its limiting value is exponential with coverage (see eq 1 of text).

atoms are able to pass both slots and reach the target. At lower rotation speeds, both metal atoms and line-of-sight radiation are blocked, allowing the background signal due to scattered radiation on the sensor to be easily measured and subtracted from the deposition signal.

The beam flux was monitored using a quartz crystal microbalance. Precise calibration of the microbalance is made by measuring the heat signal generated by depositing metal atoms onto a thick film of the metal as substrate and equating this heat to the tabulated molar enthalpy of formation of the bulk metal. For both calcium and chromium, a stable asymptote was reached at high coverages on the polymer film, which could reasonably be assigned to metal adsorption on metal. For copper, the situation was more complex, as is discussed later.

Molar heats of reaction are calculated with the assumption that the incident metal atoms condense with unit sticking probability on the polyimide substrate. An accurate radiotracer study of [110]Ag on room-temperature PMDA-ODA found that silver atoms have a sticking coefficient greater than 0.95, with the expectation that more reactive metal atoms would have sticking probabilities very near unity.[5] However, when discussing the calorimetric data, we will consider whether low reaction heats are indicative of nonunit sticking coefficients.

The measured calorimetric heats are expressed as an enthalpy of adsorption directly comparable to standard enthalpies of formation, by correcting for the kinetic energy of the thermal atom source and the gas-phase work of compression of the standard enthalpy. This procedure is described in ref 4. The kinetic energy of the atom beam, on the order of just a few percent of the reaction heat, is estimated from the temperature of the oven source and the energy dependent transmission of the velocity selector.

Results and Discussion

Representative curves for the reaction heats of calcium, chromium and copper on polyimide are shown in Figure 1. For calcium and copper, the standard deviation in the initial heat for several different trials of each was 30 kJ/mol. The chromium results showed more scatter, giving a standard deviation over five trials of 80 kJ/mol, with a mean initial heat value of 125 kJ/mol. Due to its relatively large sublimation enthalpy, the chromium experiments were performed with a lower deposition flux than those of the calcium and copper experiments, yielding about one-tenth as large an absolute signal strength.

Calcium/Polyimide Interface. As shown in Figure 1, the reaction enthalpy for calcium on polyimide at low coverages is over 540 kJ/mol and extrapolates to an initial value of greater than 600 kJ/mol at zero coverage. This indicates there is very strong binding of the isolated metal atoms. By comparison, theoretical values for the dissociation energies of some strongly bound calcium complexes are 800 kJ/mol for the bis(cyclopentadienyl) complex $CaCp_2$[6] and 450 kJ/mol for the disuperperoxo complex $Ca(O_2)_2$.[7] Calorimetry by itself does not provide bond structural data but should prove an extremely useful reference for quantum chemical calculations which do. In a simplistic analysis, the heat data are consistent with the formation of a π-bonded sandwich complex similar to the aforementioned, since those complexes were found to be quite ionic and the estimated electron affinity of PMDA-ODA (1.5 eV[8]) is intermediate to the values for molecular oxygen and the cyclopentadienyl radical (0.45 and 1.80 eV, respectively[9]).

The decrease in adsorption heat with coverage differs from previously reported calorimetric measurements for Pb on Mo[10] and Ag on Si.[11] In those systems, the decrease is almost linear, an affect associated with mobile precursor adatoms that are able to fill the first strongly absorbed monolayer before 3-D growth or clustering occurs. Figure 2 shows that the change of the differential heat signal with increasing calcium coverage on polyimide follows an almost perfect exponential decay toward its high coverage value. This behavior strongly suggests that there are a finite number of strong binding sites available on the substrate, that the fraction of calcium atoms in each pulse that bind to these sites is simply proportional to the fraction of the sites which have not yet been occupied, and that the calcium atoms which do not find unoccupied sites form metal clusters with a condensation energy approximately equal to the bulk heat of condensation observed at higher coverages. Then, the number of unoccupied sites follows a first-order decay with the

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amount of metal deposited, and the net heat of reaction is described by

$$\Delta H_{\text{diff}}(t) = (\Delta H_0 - \Delta H_{\text{bulk}})\exp\left[\frac{-t}{t^*}\right] + \Delta H_{\text{bulk}} \qquad (1)$$

In this equation, t is the amount of calcium deposited, and t^* is the amount of calcium equal to the number of high-energy binding sites on the polyimide substrate; ΔH_0 is the heat of reaction at the binding sites, and ΔH_{bulk} is the tabulated heat of condensation of calcium. The significance of the high quality of fit, seen in Figure 2, is that the Ca atoms are apparently unable to move about the surface and sample reacted sites before finding an unreacted site.

The intercept of the line gives $\Delta H_0 = 610$ kJ/mol. The slope gives a surface density of binding sites of t^* which equals 4.7 nm^{-2}. The surface monomer density of spin-coated PMDA-ODA films will depend on the degree of surface roughness and crystallinity and is typically estimated at about 1.3 nm^{-2} or higher.[12] It is tempting to suggest that there are four calcium atoms bound per PMDA-ODA monomer unit, equivalent to the number of carbonyl moieties of the polymer. However, if there is significant charge transfer involved in the bonding, then the high constant binding energy inferred from the calorimetric data would argue against such a dense coordination. Instead, the number of binding sites may indicate the degree of surface roughness or of penetration by the calcium atoms into the polyimide. Limited diffusion away from the surface has been observed for calcium on other polymers.[13,14]

Copper/Polyimide Interface. The adhesion of deposited copper films on clean polyimide surfaces is known to be poor, an indication of limited copper–polymer reactivity. Studies show the growth morphology of copper on polyimide is dominated by surface diffusion and metal cluster formation.[15] At room temperature, copper does not substantially diffuse into the bulk polymer.[16]

The data of Figure 1 show that the reaction enthalpy increases steadily with increasing coverage. Indeed, the calorimetric technique should be sensitive to changes in the size and surface energy of the metal clusters formed, which create a difference between the condensation heat at a given coverage and the bulk heat of condensation. Similar behavior is observed in calorimetric measurements of MgO substrate metallizations.[18] While our analysis is not as thorough regarding the effect of size dependency of the cluster surface tension or of the cluster/substrate adhesion energy, we show the calorimetric data are still able to reveal fine details of the growth mode and cluster density of copper on polyimide.

In the case of small clusters of uniform size, if the strength of the interaction of the copper atoms with the polyimide were negligible, then the integral heat of condensation could follow
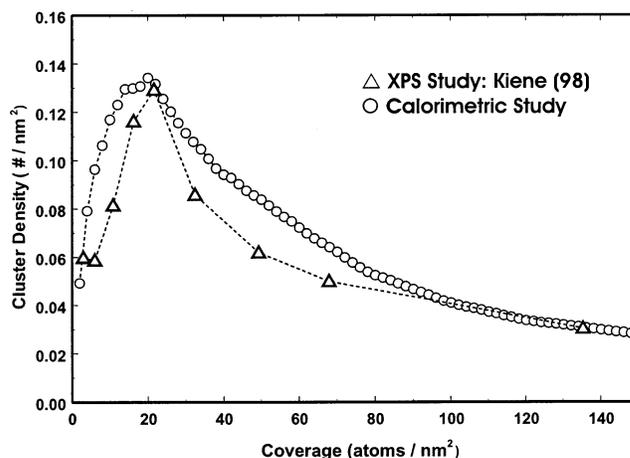

Figure 3. Copper on polyimide cluster density as a function of metal coverage based on calorimetric data and as reported by Kiene based on XPS data.

the same size-dependent binding energy found in gas-phase clusters:[17]

$$\text{BE}(N) = \text{BE}_{\text{bulk}} + 2^{1/3}(1/2D_{\text{e}} - \text{BE}_{\text{bulk}})/N^{1/3} \qquad (2)$$

where D_{e} is the known[9] binding energy of the metallic dimer, and N is the cluster size in atoms (equal to the metal coverage t divided by the cluster density, N_{c}). Kiene et al.[19] have used XPS data to study the cluster diameter of copper films grown on PMDA-ODA polyimide at room temperature. They report a uniform cluster diameter of 4–4.7 nm, depending on deposition flux, for a metal coverage of 1.6 nm (136 atoms/nm^2). From their data, we estimate a cluster diameter of 4.5 nm at our deposition flux, and based on eq 2, the copper binding energy would be 330 kJ/mol, still slightly less than the limiting bulk value of 337 kJ/mol. The absolute accuracy of our experiments is not sufficient to distinguish this 7 kJ/mol difference. We use a value of 330 kJ/mol at 136 atoms/nm^2 to calibrate the instrument rather than the bulk value at higher coverages because even for copper depositions up to 800 atoms/nm^2 the differential heat does not reach a constant value. In fact, at coverages around 500 atoms/nm^2, there is a large excursion of the heat which we attribute to coalescence of metal islands and the filling in of a continuous metal film.

The calorimetric data can be integrated over coverage and so used in a straightforward manner with eq 2 to estimate the effective cluster island diameter or the cluster density per unit area as a function of metal coverage. As seen in Figure 3, the reaction heat is able to qualitatively reproduce the XPS data of Kiene et al.[19] over the entire coverage range, with the single fixed calibration point at 136 atoms/nm^2. Both methods assume a uniform cluster diameter at any given coverage. The growth mode revealed is also seen in similar systems of Cu on benzocyclobutene polymer[20] and Au on TiO$_2$[21] and involves adjacent metal clusters growing into each other with increasing deposition and reforming into compact spheres as they coalesce. The general agreement of the XPS and calorimetry derived data substantiates our assumptions that the reaction heat can be

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accounted for by copper–copper bonding without significant contribution from copper–polyimide bond formation and with unit sticking of incident atoms.

Chromium/Polyimide Interface. Chromium is used as a reactive underlayer to promote adhesion of more inert metals such as copper onto polymeric substrates. However, the initial reaction enthalpy observed here for chromium on polyimide is surprisingly small. It may be considered that this reveals a low initial sticking coefficient for the metal atoms incident on the polymer, followed by a substantial stepwise increase at higher coverages. However, there have been many studies of XPS intensity as a function of exposure time for chromium deposition on PMDA-ODA, and no such effect has been reported. On the contrary, the attenuation of polyimide C(1s) emission as a function of calibrated exposure[22] implies that the chromium sticking coefficient is unity.

The mean initial heat value is 125 kJ/mol, with a relatively large standard deviation of 85 kJ/mol. The data shown in Figure 1 are representative of the three trials which most closely reproduced each other. The data clearly indicate that the reaction product is determined kinetically, since the more exothermic process of cluster formation does not proceed immediately as that for copper deposition. The heat observed is less than that expected for complex formation with chromium[23] and would not typically be considered large enough a binding energy to prevent diffusion or even desorption of the adatom. This can be resolved if the reaction at low coverage involves an irreversible change in the polymer structure, such that the chromium atom is strongly bound but the overall reaction has a low net exothermicity due to the cost of polymer bond disruption.

One model of PMDA-ODA metallization involves metal-oxide formation by the abstraction of oxygen atoms from the polymer, and based on the correlation of metal/polymer reactivity with the standard enthalpies of metal-oxide formation, Chou et al.[24] estimate that the free energy change for chromium reaction with PMDA-ODA is 300–400 kJ/mol. However, the calorimetric data suggests that the reaction products formed are actually substantially higher in energy than the bulk metal-oxide

and also that the assumption of a constant difference between reaction enthalpy and bulk metal-oxide formation enthalpy is incorrect, as the measured heat for chromium then implies that the reaction of nickel atoms with PMDA-ODA would be endothermic, whereas they are known to form a reactive pair.

The rise in heat after 10 atoms/nm^2 is easily attributed to metallic chromium growing on the reacted chromium. The relative abruptness of the transition implies that the chromium metal wets the reacted layer, rather than forming highly dispersed clusters as in the copper data. If the metal condensation and polymer reaction are each occurring with constant molar enthalpy in the region between 10 atoms/nm^2 and 30 atoms/nm^2, then the amount of chromium incorporated into a reacted layer with the polymer is just over 20 atoms/nm^2, close to a single atomic layer of the bulk metal.

Conclusion

Calorimetry has been used to observe the reaction enthalpy of polymer metallization. Three metals, copper, calcium, and chromium, were studied. Each metal was deposited on PMDA-ODA polyimide substrates with dramatically different results.

The calcium/polyimide system has not been reported on before. Our results indicate the presence of a single, strong calcium–polymer interaction. The binding energy of this metal–polymer complex was estimated at 610 kJ/mol, with a density of binding sites of 4.7 nm^{-2}. The copper results are consistent with the established picture of film growth by metal cluster formation. Cluster densities derived from the reaction enthalpies were compared with published data derived from XPS signal ratios. The correlation over the full range of available coverages confirm that copper–copper and not copper–polyimide interaction dominates the heat evolution. For the first monolayer of chromium deposition, the heat of adsorption is below 125 kJ/mol. This is attributed to the formation of a reacted layer with irreversible cleavage of chemical bonds of the polymer. After 10 atoms/nm^2 deposition, there is a relatively sharp transition of heat to 400 kJ/mol, indicating growth of a continuous metallic film on the reacted layer.

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