metal surface; deposition was seen on the glass wall directly under the lamp beam. However, an induction period for deposition on the glass wall was observed which increased with decreasing substrate temperature.

Figure 3 shows typical films deposited at a precursor partial pressure of 50 mTorr. The surface morphology showed differences in grain structure as a function of temperature. Films deposited at 200 °C (Figure 3, left) had an average surface grain structure of approximately 2.0 μm with well-connected grain boundaries. Despite the large grain structures (>1 μm), the films were specular, which suggested that they were smooth. Such films with large grain structures can exhibit high electromigration resistance.[21] This is an important reliability issue for devices operating at high frequency and high current density.[22] The high density and purity of the films were reflected in the near bulk resistivity (2.0–2.1 μΩ cm) obtained for films deposited above 170 °C. However, higher resistivities were measured for films deposited below 170 °C (Table I) where the morphology changed from well-connected grains to near spherical grains (~0.2 μm) which were connected at only a few points (Figure 3, right). Because all of the films deposited in the cold-wall reactor were high-purity copper as determined by AES, this demonstrates the impact of film morphology on the electrical characteristics of the deposited films.

In summary, hot-wall CVD from (hfac)copper(I) alkyne compounds produces pure copper films via disproportionation over the temperature range 150–250 °C. In a cold-wall differential reactor, high deposition rates of up to approximately 1 μm/min were achieved, but above 200 °C the deposition rate did not increase with temperature and was feed-rate-limited under the conditions employed. The activation energy for CVD of copper from (hfac)Cu(2-butyne) was 23 (2) kcal/mol. The film morphology had a direct impact on the resistivity of the films. Dense well-connected grains were obtained for temperatures above 170 °C, with grain structure increasing with temperature. Further experiments are underway to determine the effect of precursor partial pressure on the deposition rate and to understand the chemical significance of the activation energy.

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**Supplementary Material Available:** SEM and AES data of copper films deposited from (hfa)Cu(2-butyne) (11 pages). Ordering information is given on any current masthead.

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## Contact Electrification: Ion Transfer to Metals and Polymers

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The contact and separation of two different surfaces cause them to charge with the opposite sign. Because it is a surface phenomenon, changes in the composition of either surface affect both the sign and magnitude of the charge. The charging mechanism with polymers has been attributed to the transfer of ions[1-4] and electrons.[5-7] Thus, salts or ionomers[2-7] are often added to polymers to control the charge. In particular, ionomers are useful for studying the charging mechanism because one of the ions is covalently bonded to the polymer, while the accompanying counterion can be mobile. Therefore, an ionomer and a molecular salt with the same ions will charge differently in an ion-transfer process but will charge similarly for an electron-transfer process because the structural difference due to binding to the polymer has a marginal effect on the ionization potentials and electron affinities.

Contact electrification studies with ionomers have been carried out using a metal (conductive)[5-7] or a polymer (insulative)[3,4] as the second surface. Methyltriarylphosphonium arylsulfonate salts were employed where, in one case, the phosphonium cation was attached covalently to the ionomer chain while in the other, the arylsulfonate anion was attached.[5-7] Powders containing either ionomer charged positive against a metal surface (independent of ion mobility) and the charge increased with the ion content in the blend. A correlation was found between the charge, the HOMO levels, and the redox potentials for a series of substituted arylsulfonate ions. Thus, electron transfer was proposed as the mechanism for charging. Electron transfer has also been proposed for the development of charge with substituted polystyrenes,[8] salicylaldehyde anils,[8] and polymer-bound triphenylphosphines[9] when contacted with metal particles. The proposal is again based on correlations between the charging behavior and the calculated $\pi$ energy levels for the aromatic structures[8] and work functions.[9]

The case for ion transfer has been strengthened by two separate studies. In one, a blend of a styrene–butyl methacrylate copolymer and an ionomer containing poly(styrene-*co*-*N*-methyl-4-vinylpyridinium toluenesulfonate) ([P]-PyMe$^+$OTs$^-$) was contacted with another polymer (insulative).[3,4] The ionomer-blended powder developed a positive charge, and the charge again increased with the ionomer content. Furthermore, the OTs$^-$ was observed by XPS on the surface of the second polymer after contact and removal of the powder. This evidence supports the ion-transfer mechanism (OTs$^-$ transfer). In the charging experiments between cetylpyridinium bromide blended with polystyrene and indium,[10] the polymer acquired a positive charge. Both ions were detected by SIMS on the negatively charged indium surface after contact; however, the Br$^-$ was in large excess of the cation. Again, the direct observation of the transferred ion on the contacted surface is strong evidence for ion transfer. Since the conductivity

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**Table I. Contact Charge and XPS Results**

| 8–12-μm powder | | | 140–200-μm beads, at. % (XPS)[a,b] | | | | |
|---|---|---|---|---|---|---|---|
| ions in powder | salt concn, μmol/g | $\Delta Q/\Delta M$, μC/g | C | O | S | N | Na |
| Second Surface: Bare Spherical Beads (Conducting) | | | | | | | |
| no powder contact | | | 27.39 | 72.61 | nd[c] | nd[c] | nd[c] |
| no ions | 0 | −3.7 | | | | | |
| [P]-PyMe$^+$OTs$^-$ | 2.6 | 16 | | | | | |
| [P]-PyMe$^+$OTs$^-$ | 5.2 | 45 | | | | | |
| [P]-PyMe$^+$OTs$^-$ | 26 | 56 | 62.9 | 36.8 | 0.23 | nd | |
| [P]-PyMe$^+$OTs$^-$ | 63.0 | 62 | 63.2 | 36.6 | 0.28 | nd | |
| 4-Et-PyMe$^+$OTs$^-$ | 51.0 | −2.1 | 60.4 | 38.1 | 1.18 | 0.28 | |
| [P]-PhSO$_3^-$Na$^+$ | 13.2 | −20 | | | | | |
| [P]-PhSO$_3^-$Na$^+$ | 21.9 | −25 | 48.2 | 36.4 | nd | nd | nd |
| Second Surface: Bare Irregular Beads (Conductive) | | | | | | | |
| no powder contact | | | 45.3 | 49.9 | 0.9 | 0.18 | nd |
| no ions | 0 | −11 | 49.6 | 39.8 | 0.9 | nd | |
| [P]-PyMe$^+$OTs$^-$ | 2.6 | 2.7 | | | | | |
| [P]-PyMe$^+$OTs$^-$ | 5.2 | 37 | | | | | |
| [P]-PyMe$^+$OTs$^-$ | 15.6 | 55 | | | | | |
| [P]-PyMe$^+$OTs$^-$ | 36.4 | 72 | 69.5 | 29.3 | 1.16 | nd | |
| 4-Et-PyMe$^+$OTs$^-$ | 51.0 | −1.0 | 58.0 | 39.3 | 1.92 | 0.74 | |
| [P]-PhSO$_3^-$Na$^+$ | 13.2 | −13 | | | | | |
| [P]-PhSO$_3^-$Na$^+$ | 21.9 | −16 | 48.4 | 39.6 | 0.8 | | 0.03 |
| Second Surface: Coated Irregular Beads (Insulating)[3] | | | | | | | |
| no ions | 0 | 0.7 | 47.7 | 7.70 | nd | 1.85 | nd |
| [P]-PyMe$^+$OTs$^-$ | 2.6 | 5.5 | | | | | |
| [P]-PyMe$^+$OTs$^-$ | 5.2 | 26.7 | | | | | |
| [P]-PyMe$^+$OTs$^-$ | 15.6 | 53.8 | | | | | |
| [P]-PyMe$^+$OTs$^-$ | 36.4 | 70 | | | | | |
| [P]PyMe$^+$OTs$^-$ | 52.0 | 72 | 58.3 | 7.68 | 0.19 | 1.04 | |
| 4-Et-PyMe$^+$OTs$^-$ | 51.0 | 5.4 | 50.5 | 8.00 | 0.68 | 2.3 | |
| [P]-PhSO$_3^-$Na$^+$ | 13.2 | −13 | | | | | |
| [P]-PhSO$_3^-$Na$^+$ | 21.9 | −14 | 49.6 | 7.56 | nd | | 0.07 |

[a] Analysis after rolling and removal of powder. [b] Peak positions and cross sections for XPS signals: C, 284.6 eV (1.00); O, 532.2 eV (2.494); S, 167.4 eV (1.793); N, 401.7 eV (1.678); Na, 1072 eV (8.52). [c] Not detected; less than 0.02.

of the second surface is one difference between our previous studies[3,4] and those from other laboratories, we extended our charge studies to metal beads to eliminate this difference.

[P]-PyMe$^+$OTs$^-$, 4-ethyl-*N*-methylpyridinium toluenesulfonate, (4-Et-*N*-MP$^+$OTs$^-$), and the styrene-*co*-butyl methacrylate random copolymer were available from previous studies.[3,4] Powders of the copolymer/ionomer (or salt) blends were prepared by melt mixing the components, milling the solid mixture, and size classifying the powder as previously described.[3,4] The particle sizes were measured using a Coulter multianalyzer and were in the range 8–12 μm in diameter. For the charging studies, the powder was first rolled in a can with metal beads (mix ratio either 2.5% with 140 μm irregularly shaped or 1% with 200 μm spherical) for 30 min, during which time the charge builds up to an equilibrium level (by ca. 20 min). Therefore, the charge is an equilibrated value, and differences between samples reflect equilibrium charge transfer and not the rate of transfer. The powder was then blown off from the two component mixtures using a Faraday cage, and the $\Delta Q/\Delta M$ values are calculated from the measured charge and weight loss of the cage.[3,4] Normally, >95% of the smaller particles are removed from the larger ones.

As seen in Table I, the powders containing 2–50 μmol/g of PyMe$^+$OTs$^-$ charge increasingly positive with the ion content. Parallel charge levels were attained with the two irregular bead surfaces (polymer coated and bare). Thus, the metallic/conductive nature of the beads has no effect on the charge. The higher charges observed with the bare metal spherical beads may simply reflect a consistent difference in the powder/bead surface area ratio. A 60 μC/g charge on the powder corresponds to 1.5 μC/g charge on the spherical beads and to a surface charge (ion) density of $18 \times 10^{10}$ charges (ions)/cm$^2$. This corresponds to a 0.2% surface coverage since a monolayer of ions with ca. 10 Å$^2$ footprint has $10^{14}$ ions/cm$^2$.

Beads recovered after contact and separation from the powder were analyzed by XPS for ions from the powder, S for OTs$^-$ and N for *N*-MP$^+$. The beads were supported on In foil, and an SSX-100 Model 05 XPS spectrometer with a 300-μm spot was used. Low-energy electrons were supplied to the sample, as required, to neutralize surface charging. The binding energies were referenced to the main carbon peak, taken as 284.6 eV. The surface compositions of these powders from XPS have been reported,[4] and the powder containing 26 μmol/g PyMe$^+$OTs$^-$ had 93.6% C, 6.4% O, 0.04% S, and <0.02% N (below the detection limit),[4c] which compare well with the calculated bulk composition, 93.4% C, 6.4% O, 0.033% S, and 0.033% N. Although a signal for nitrogen was not observed with this sample, it was observed with the expected size for samples containing higher methylpyridinium OTs$^-$ content.[4] The elemental analyses of the bare beads are listed in Table I along with data from previous studies. Signals for S and N were not detected on the bare metal beads before contact with the ionomer blend powder. After contact and separation from the powder, only S for OTs$^-$ was present but no N for the pyridinium ion in the ionomer. Similar results were observed previously with the polymer-coated beads; unfortunately the coating contained nitrogen, which introduced ambiguity.[3,4] The OTs$^-$ found on the metal beads was not due to large fragments of the powder because the S/C ratio on the bead surface (0.0036) was ca. 10 times the ratio on the powder surface (0.0004 for 26 μmol/g of salt), and because nitrogen was not found on the beads after contact with the powder. Thus the sulfur signal reflects the selective transfer of OTs$^-$ to the beads which became negatively charged while retention of the methylpyridinium ion gave rise to the positive charge on the powder. Assuming a monolayer coverage of organics on the beads, the 0.2% S approximates the surface ion density calculated above.

Changing the mobile ion from OTs$^-$ to Na$^+$ changes the sign of the charge transferred, and Na$^+$ (but not S) is detected on the beads. This is seen with the powders containing the partially sulfonated polystyrene sodium salt ([P]-PhSO$_3^-$Na$^+$).[4,11,12] [P]-PhSO$_3^-$Na$^+$, with 438 μmol/g of PhSO$_3$Na, was used in the blends. The surface composition of the powder containing 21.9 μmol/g of PhSO$_3$Na was 93.37% C, 6.69% O, 0.03% S, and 0.02% Na, which again compares well with the calculated bulk values, 93.5% C, 6.35% O, 0.03% for S and Na. Against the metal oxide surfaces the charge varies widely and a small amount of Na$^+$ is observed on only one surface. This possibly reflects the complication with moisture associated with the hydroscopic Na$^+$ salts. With the molecular salt 4-Et-*N*-MP$^+$OTs$^-$ both the cation and anion are observed on the beads after contact, and smaller charges (closer to zero) are observed, reflecting a compromised charge due to the transfer of both ions in different amounts. Against the bare spherical beads, the charge is effectively that of the unblended copolymer even though there are many ions on the beads. Ion aggregation and accumulation of the molecular salts on the powder surface[3,4,10] are partially responsible for the difficulty in interpreting their charging behavior.

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Ions clearly transfer between the surfaces during contact. The dependence of the charge of ion content, the correspondence between the sign of the transferred charge and the mobile ion (– for $OTs^-$ and + for $Na^+$), and the parallel relationship between the $\Delta Q/\Delta M$ values for both the coated and the bare metal surfaces (independent of conductivity) are strong evidence for the ion-transfer mechanism for charging. Ion transfer is consistent with the insensitivity of the $\Delta Q/\Delta M$ to the nature of the second surface, while electron transfer would be strongly influenced by the change in conductivity. Furthermore, these ions (or polymers) do not oxidize or reduce under ambient conditions.[13] Although these results do not disprove the electron-transfer process, there is also no need to invoke it. The occurrence of parallel electron and $OTs^-$ or electron and $Na^+$ exchange processes for charging would be highly coincidental. The relationship between the sign of the charge and of the mobile ion is observed with an acrylate resin with pendent sulfonic acid groups (mobile $H^+$)[14] but not with [P]-$PhSO_3^-Ph_4P^+$ (large, less mobile cation).[7] When the mobility of the principal ions is low, the exchange of extraneous ions and/or ions from moisture will occur to produce the charge which may be the case with these materials which are reported to have minor amounts of ionic impurities.[6] When both ions are mobile[3] or united as with betaines,[15] the situation is even more complicated.

Finally, $OTs^-$ may not be the only ion transferring during contact, and it may be accompanied by the transfer of protons and hydroxide ions from the dissociation of moisture.[16,17] Unlike metal–metal charging where electron transfer has been demonstrated,[18-20] we feel that when mobile ions are present, charging results from the transfer of ions, for polymer–polymer and for polymer–metal contacts.

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## Mixed Methyl- and Ethylzinc Complexes with Diethylselenocarbamate: Novel Precursors for ZnSe

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Zinc selenide is potentially a particularly important II/VI material having applications in a wide range of roles from blue LEDs[1] to infrared optics.[2] Thin films of zinc selenide can be grown in a number of ways including chemical vapor deposition (CVD),[3] metalloorganic chemical vapor deposition (MOCVD; using precursors such as dimethylzinc[4] or an adduct[5] and usually $H_2Se$ as the selenium source), and molecular beam epitaxy (MBE) from elemental sources.[6]

Developing single-molecule precursors, in which both the chalcogen and the metal are contained within a discrete molecule presents a considerable challenge to the chemist. Sources of this kind have been prepared for III/V materials such as InP and GaAs by Bradley and Faktor[7] and Cowley and Jones.[8] There have also been a number of reports on the deposition of sulfides from single-molecule sources such as thiophosphinates,[9] thiocarbamates,[10] and mixed-metaldialkylthiocarbamates.[11] The latter class of compounds are dimers of the formulae $RMS_2CNR'_2$ (R or R' = Me or Et; M = Zn; R = Me, R' = Et, M = Cd). An X-ray structure of $[MeZnS_2CNEt_2]_2$ reveals each dithiocarbamate chelates one zinc atom and bridges to the next. Complexes of cadmium and zinc with very bulky alkyl sulfides, selenides, and tellurides have also been used as single-molecule precursors for some II/VI materials.[12]

In the present communication we report that the new compounds $RZnSe_2CNEt_2$ (R = Me or Et) have been successfully used to deposit thin films of ZnSe. We believe these are the first successful single-molecule precursors for thin films of ZnSe.

The insertion of $CS_2$ into the M–N bond of a mixed alkylthiocarbamate to produce a compound of the stoichiometry $RMS_2CNEt_2$ was first reported by Noltes[13] (M = Zn, R = Et):

$$MR_2 + HNEt_2 \rightarrow RMNEt_2 + RH \xrightarrow{CS_2} RMS_2CNEt_2$$

M = Zn, R = Me or Et
M = Cd, R = Me

We have earlier confirmed the above chemistry for diethylzinc and extended such reaction to both dimethylzinc and -cadmium.[11] A different strategy was adopted for the synthesis of the selenocarbamate derivatives in order to minimize the handling of $CSe_2$, which is a particularly noxious material. $CSe_2$ was prepared by the literature method[14] and immediately converted to the *N,N'*-diethylselenocarbamate as the diethylammonium salt.[15] This was then used to prepare bis(diethylseleno-

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