Chemistry of Materials 1989, 1, 291-292

Chemical Basis for Adhesion. Interaction of Chromium with Polyimide: Model Studies

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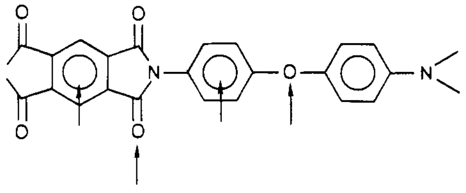
Received November 7, 1988

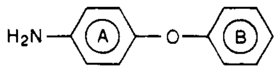
The relationship between the macroscopic properties of metal–polymer and semiconductor–polymer interfaces and the nature of the chemical bonds formed at the interface are of fundamental importance, especially to the electronics industry. For example, the very large scale integration of devices (VLSI technology) necessitates the use of multilayered structures at the chip level and for packaging.[2] Such structures are usually fabricated by using alternate metal and insulating layers and thus incorporate metal–insulator interfaces throughout the structure. Hence, good adhesion of the metal to the insulator surface is of critical importance, and, to this end, a detailed understanding of the relationship between chemical bonding and adhesion quality will provide new opportunities for optimizing metal–polymer adhesion.

Polyimide (PI, I) derived from pyromellitic dianhydride and *p,p′*-oxydianiline has emerged as the material of choice as an insulating and pattern-delineating matrix in the area of VLSI technology.[3] Consequently, the problem of adhesion between PI and metals is of paramount importance. The adhesion of metals to PI vary considerably:[4] Cu displays poor adhesion while Cr adheres strongly to PI surfaces. The reason for this difference between Cu and Cr has remained unclear. On one hand, it has been postulated[5] on the basis of several spectroscopic studies that Cr on deposition on PI interacts strongly with the carbonyl groups present while an analogous interaction is absent for Cu. On the other hand, a theoretical study of the interaction of Cr with a PI model compound concluded[6] that Cr forms a π-arene complex with the anhydride ring. Since Cr atoms are deposited in the zerovalent state, a strong interaction with arene rings would be consistent with the tendency for Cr(0) to form stable π-arene complexes.[7] Nevertheless, the choice of the anhydride ring as the bonding site for Cr is surprising. Electron-rich arenes generally form stronger π-arene complexes,[8] and, on this basis, the ligating ability of the anhydride ring should be significantly *inferior* to that of the other phenyl group present in PI. Herein, we describe the results of our study of the interaction of the Cr(0) fragment, $Cr(CO)_3$, with several PI model compounds. Our results serve to delineate, for the first time, the relative preference of Cr(0) for the various reactive sites on PI (I) and demonstrate that *neither* the carbonyl groups *nor* the anhydride ring is the *thermodynamically* preferred bonding site for Cr(0) in the $Cr(CO)_3$ fragment.



I

To probe the reactivity of Cr(0) vis-à-vis the different reactive sites on PI, the products formed by the reaction of $Cr(CO)_3(MeCN)_3$[9] with the model compounds **1–5** were identified. The reactions were generally carried by the addition of 1 equiv of the Cr(0) precursor to the organic substrate in tetrahydrofuran (THF) or Bu_2O following which the reaction mixture was heated to reflux for 48 h. The product obtained was isolated through conventional procedures and characterized by mass, IR, and ^1H NMR spectroscopies. In all cases, including **5**, the only identifiable Cr-containing species formed was the π-arene complex, (arene)$Cr(CO)_3$. The most characteristic ^1H NMR spectral feature of this complex was the substantial upfield shift of the resonances of the protons of the coordinated arene ring.



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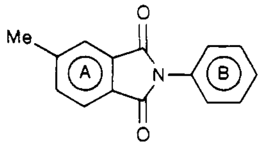

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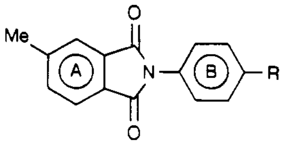
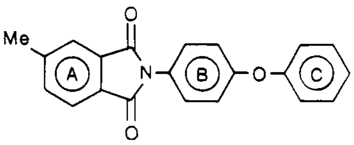


3a, R = Et
b, R = *t*-Bu



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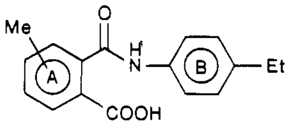

5

Ring A was the exclusive binding site for the metal in the Cr(0) complex formed with **1**. This was indicated by the presence of doublets at 4.8 and 3.8 ppm (J = 6.8 Hz) in the ^1H NMR spectrum. Furthermore, ^1H NMR spectroscopy at elevated temperatures did not indicate any movement of the $Cr(CO)_3$ fragment from ring A to ring B, thus indicating that the former ring was the thermodynamically preferred binding site. Since ring A is more electron rich than ring B (two donor substituents, NH_2 and OPh, versus one, OPh), this result indicates that the Cr(0)

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0897-4756/89/2801-0291$01.50/0

fragment prefers to bind to the more electron-rich site. With **2**, the Cr(0) fragment was found to bind to both rings A and B with a ~2:1 preference for the *latter* ring. Binding to ring A was indicated by the presence of two doublets (6.5 and 5.7 ppm, J = 6.2 Hz) and a singlet (6.2 ppm) of equal intensities in the ^{1}H NMR spectrum. Binding to ring B was shown by the presence of a doublet (6.0 ppm, J = 7.1 Hz), a doublet of doublet (5.6 ppm, J = 7.1, 6.1 Hz), and a triplet (5.4 ppm, J = 6.1 Hz) in the intensity ratio of 2:2:1. Replacing **2** with **3a** and **3b**, which have electron-releasing alkyl groups on ring B, resulted in the formation of arene complexes in which the $Cr(CO)_3$ fragment was now bound to rings B and A in a 4:1 ratio. The preference of Cr(0) for ring B in compounds **2** and, especially, **3a,b** correlates well with the observation that the ^{1}H NMR resonances for the hydrogens on ring B occur upfield of ring A in the free ligand, indicating that the electron density in ring B is higher than in ring A. In compound **4**, ring C is the only arene ring lacking electron-withdrawing substituents and would be expected to be the preferred binding site. Indeed, the π-arene complex of ring C was the only Cr(0) complex isolated in the reaction of $Cr(CO)_3(MeCN)_3$ with **4**.

Finally, the amic acid functionality is often present in PI samples because of incomplete ring closure.[10] Thus, it was of interest to verify whether Cr(0) would form arene complexes even in the presence of such a reactive functionality. The product observed in the reaction of *excess* Cr(0) with **5** was a species in which one $Cr(CO)_3$ fragment was π-bound to each of the two rings A and B.

Although the π-arene complex was the only Cr-containing species isolated in the reactions described above, it was possible that other Cr species were also being formed but did not survive the workup and isolation procedures. To test this possibility, we monitored the progress of the reaction of $Cr(CO)_3(MeCN)_3$ with **3a** and **3b** by ^{1}H NMR spectroscopy using THF-d_8 as the solvent. However, except for the π-arene complexes, no other organometallic or organic species was detected.

The results of our study of the interaction of $Cr(CO)_3(MeCN)_3$ with compounds **1**–**5** lead to the following conclusions: (a) Cr(0) prefers to form π-arene complexes (even with electron-deficient arene rings) rather than react with oxygen functionalities, including the reactive carboxylic acid functionality; (b) the tendency to form a π-arene complex increases with increasing electron density on the ring. On the basis of these conclusions, it would appear that the *thermodynamically* preferred binding site for Cr(0) in PI is the ring derived from *p,p′*-oxydianiline rather than the anhydride ring or the oxygen functionalities. Note, however, that our study does not address the question of the relative *kinetic* accessibility of the different binding sites on PI. Thus, upon deposition on PI, the Cr atoms may well bind to the carbonyl groups on PI if these are more accessible from a kinetic standpoint. Our study does, however, indicate that if π-arene complexes are formed, these would be likely to involve the amine fragment rather than the anhydride ring.

Although our conclusions are derived from the study of (arene)$Cr(CO)_3$ complexes, there are no compelling reasons to believe that they would not be valid for other (arene)-Cr(0) species such as those which may form through the interaction of Cr atoms with PI.[11] Unlike Cr(0), Cu(0) does not form stable π-arene complexes,[12] and this may be one reason why the bonding between PI and Cr is significantly stronger than that between PI and Cu.

Acknowledgment. Support of this research by the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-84ER13295), is gratefully acknowledged.

Registry No. **1**, 139-59-3; **2**, 85090-26-2; **3a**, 119596-19-9; **3b**, 119596-20-2; **4**, 119596-21-3; **5**, 119596-22-4; $Cr(CO)_3(MeCN)_3$, 16800-46-7; Cr, 7440-47-3; (pyromellitic dianhydride) (*p,p′*-oxydianiline) (copolymer), 25038-81-7; (pyromellitic dianhydride) (*p,p′*-oxydianiline) (SRU), 25036-53-7.

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The New Borate $Sr_3Sc(BO_3)_3$

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Received February 2, 1989

Energy efficiency has long been an important and critical issue in the development of the science and technology of solid-state lasers, particularly in high-power systems. Additional interest in efficiency and efficient crystalline laser materials has recently developed from the potential to realize new and improved laser characteristics in laser-pumped laser geometries. For example, new compounds doped with the ion Cr^{3+} are of particular interest as potentially efficient lasers for high-intensity pumping and ground-state depletion of Nd^{3+} and other laser crystals.[1]

We are involved in the systematic synthesis and study of new solid-state materials that will serve as hosts for the realization of small excited-state absorption cross sections when doped with the ion Cr^{3+}. Excited-state absorption has been reported to be the primary effect limiting the overall energy efficiency of several solid-state lasers operating from a d^3 transition-metal cation.[2,3] In this communication, we briefly describe our approach to synthesizing one class of these materials, complex scandium borates, presenting as an example the new compound $Sr_3Sc(BO_3)_3$.

The reported slope efficiency, 29%, of the laser material Cr^{3+}:$ScBO_3$[4] ranks fifth among all Cr^{3+} lasers, providing a performance that is better than would be predicted from consideration of the position (810 nm) of its maximum fluorescence intensity in the context of simple models of excited-state absorption for a d^3 cation.[1,2,5] Given the high efficiency of this material with what appear to be less than optimal optical features, it is likely that an even higher efficiency could be achieved if the characteristics of the

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