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Mercury and C₂B₁₀ Icosahedra Interaction

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ABSTRACT

We contrast the interaction of mercury with adsorbed orthocarborane films and semiconducting (dehydrogenated) boron carbide. Photoemission spectra reveal small shifts in orthocarborane (C₂B₁₀H₁₂) molecular orbital binding energies as well as the shift in mercury 5d_{5/2} shallow core level binding energies, suggesting only small interaction between mercury and the molecular film. Mercury does, however, interact with decomposed orthocarboranes i.e. semiconducting boron carbide.

INTRODUCTION

Semiconducting boron carbide represents a new class of semiconducting materials with potential applications in neutron detection and radioactive decay calorimetry [1-4]. Boron has high cross section for neutrons at lower energies while several isotopes of mercury have a high neutron cross section at higher energies [5]. The combination of mercury doped boron carbide could then be a candidate for neutron detectors over a wider range of neutron energies. Thus coadsorption of mercury and boron carbide as well as an icosahedral carborane like *closo*-1, 2-dicarbododecaborane, C₂B₁₀H₁₂ (commonly known as orthocarborane) may have some practical value.

Such studies are not, however, unique. Mercury and alkali metal mixtures with molecules have a long history in the study of non-metal to metal transitions. Alkali metal mixture with carboranes has been studied through the nonmetal to metal transition [6, 7], while iron [8-11], vanadium [9], chromium [9] and nickel [9, 12-14] doping of boron carbides is known. All of these latter transition metal dopants dope boron and boron carbides n-type.

Photoemission measurements are used here to assess if changes of the electronic properties of orthocarborane occur when mercury is co-deposited with orthocarborane. Changes in the electrical properties of the semiconducting boron carbide films reveal if mercury doping has occurred, or (in effect) indicate if there is interaction with the dehydrogenated orthocarborane.

EXPERIMENTAL

The photoemission experiments were performed in a UHV system equipped with a hemispherical energy analyzer. The photon-energy source employed was the 1-GeV Alladin ring of Synchrotron Radiation Center at Stoughton, Wisconsin. The light was dispersed by a four meter, normal incidence monochromator having the energy of 35 eV in a largely p-polarized configuration, 65° off normal. The photoemission spectra were obtained at normal emission. The light source and the electron energy analyzer had a combined energy resolution between 40 and 80 meV. All the binding energies are referenced to the Fermi energy of the clean copper substrate. The substrate was cleaned by Ar⁺ ion sputtering before each adsorption experiment and annealed at 850 K. Adsorption of orthocarborane onto the Cu (100) substrate was followed by mercury coadsorption at 180 K. The coverage was determined by the attenuation of the substrate photoemission features as was undertaken in previous work [15] including previous efforts on the coadsorption of Hg and carboranes [16]. The mercury exposure is denoted in terms of Langmuirs where 1 L = 10⁻⁶ Torr.sec. Transport measurements were undertaken for decomposed orthocarborane films between the room temperature down to 3 K. Conductance measurements were also performed for the samples under a pure ambient vapor of mercury at room temperature. The samples were kept under vacuum while the mercury is admitted into the chamber through a valve.

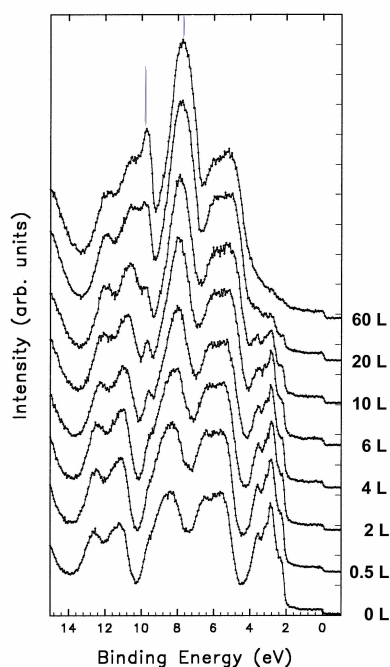


Figure 1. Photoemission spectra of one molecular monolayer of orthocarborane on Cu(100) (T=180 K) and the same film after coadsorption of Hg. The mercury induced photoemission features (7.6 and 9.6 eV) are identified (as indicated) in the figure as the Hg 5d_{5/2} and 5d_{3/2} shallow core levels.

INTERACTIONS WITH MOLECULAR CARBORANES

To compare mercury interaction with hydrogenated C_2B_{10} icosahedra, with dehydrogenated C_2B_{10} icosahedra, the electronic structure of mercury adsorption on molecular films of orthocarborane was investigated. For orthocarborane, the highest occupied molecular orbital (HOMO) appears in the photoemission spectra at an initial binding energy of 5.7 eV below the Fermi level, while the lowest unoccupied molecular orbital (LUMO) is observed at roughly 4.25 eV with respect to the Fermi level ($E-E_F$) [6,7]. This HOMO-LUMO gap is generally consistent with theory [6,7,16]. While many of the molecular orbital results in overlapping photoemission features, a number of photoemission features are easily attributable to the molecular orbitals of orthocarborane. In Fig. 1, we present the photoemission spectra of one molecular monolayer of orthocarborane adsorbed onto Cu (100) substrate at $T=180$ K before and after coadsorption of mercury. The orthocarborane molecular orbital induced photoemission features are evident at binding energies of 5.7, 6.3, 6.8, 8.2, 11.2 and 12.3 eV. The substrate copper d-bands are evident in the spectra between 2 and 4 eV binding energy.

With increasing mercury exposure to the carborane film at 180 K, the mercury induced photoemission features appear at binding energies of 9.6 eV and 7.6 eV, and are identified as Hg $5d_{3/2}$ and Hg $5d_{5/2}$ shallow core levels, respectively. The Hg $5d_{5/2}$ shallow core level and the orthocarborane features at 8.2 eV overlap, consequently the Hg $5d_{5/2}$ features initially appear broader at low mercury exposures. As seen in Fig. 2, the intensity of copper features decreases while the intensity of mercury features increases with mercury coadsorption, however, the orthocarborane intensity of Hg $5d_{5/2}$ core level remains largely unchanged. This tends to suggest that the mercury is NOT wetting the orthocarborane film.

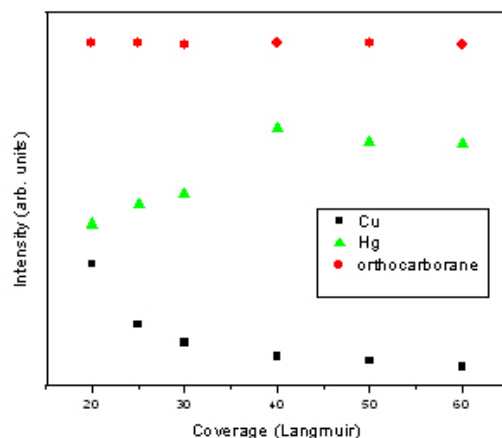


Figure 2. The photoemission intensities of the Hg $5d_{3/2}$ core level, the Cu 3d bands and orthocarborane, as a function of Hg exposure to a monolayer carborane film on Cu(100) at 180 K.

A signature of interactions between the carboranes and the coadsorbed mercury is indicated by the shifts in binding energy of both the orthocarborane photoemission features and the shallow core levels of mercury. A small increase in the mercury shallow core level binding energies concomitant with the decrease in orthocarborane molecular orbital binding energies was observed, as seen in Figure 3. The shift in binding energy of the mercury 5d level and the binding energy change in orthocarborane have same magnitudes, but opposite directions. This suggests that the coadsorption of mercury may result in a small charge transfer between the orthocarborane and the mercury. Hybridization between the mercury 5d core level and the molecular orbitals of the orthocarborane clusters is, nonetheless, indicated. The shift in binding energies of the mercury 5d core level and the molecular orbitals of the orthocarborane saturates at about 20-25 L of mercury coverage. The small shift in intensities implies that the interaction between orthocarborane and mercury is weak.

DOES MERCURY DOPE SEMICONDUCTING BORON CARBIDE?

In contrast to the result above, there appears to be interaction with the dehydrogenated C_2B_{10} molecular icosahedra. The decomposition of orthocarborane leads to the formation of a semiconducting boron carbide and is easily doped with nickel [12-14, 17]. Given the small interaction between Hg and the molecular film, at issue is whether Hg dopes the semiconducting boron carbide resulting from the dehydrogenation of orthocarborane. To address this problem, we undertook transport measurements on the decomposed orthocarborane films, i.e. semiconducting boron carbide, on an insulating substrate both in the absence and in the presence of a mercury atmosphere. If doping occurs, the semiconducting boron carbide should exhibit a significant decrease in resistivity, as observed for nickel [13].

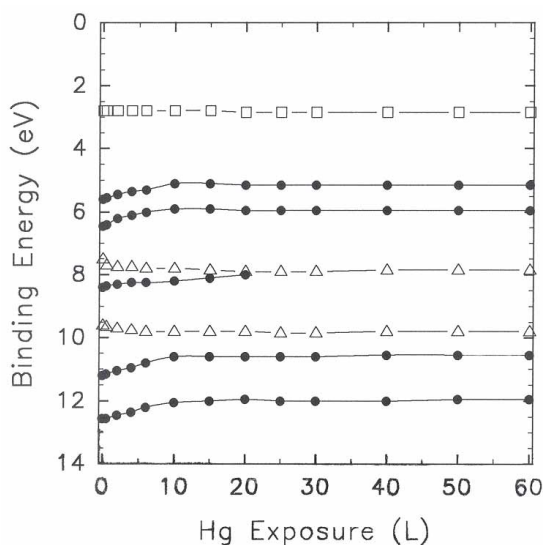


Figure 3. The binding energies of Cu (square), Hg (triangles), and orthocarborane (circle) features as a function of mercury exposure to a molecular orthocarborane film at 180 K.

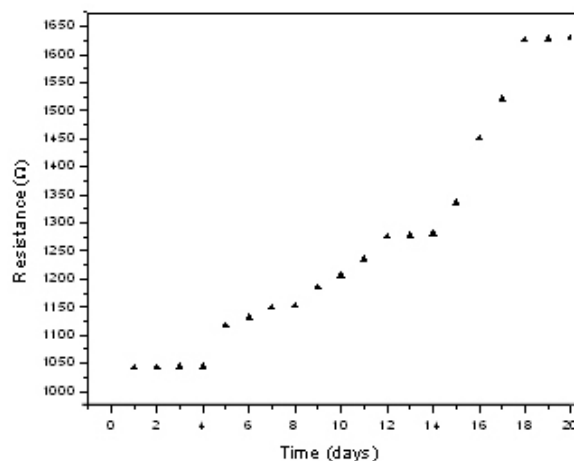


Figure 4. The resistance of semiconducting boron carbide with time, at room temperature under exposure to a mercury vapor.

The temperature dependence of semiconducting boron carbide is characteristic of a semiconductor with both intrinsic and extrinsic carriers. Following extensive exposure to mercury vapor, the semiconducting film becomes increasingly resistive at room temperature, as seen in Figure 4. This suggests that mercury is a poor conventional dopant as whatever mercury incorporation occurs, this only leads to a decrease in carriers.

CONCLUSIONS

Weak hybridization between the mercury 5d core level and the molecular orthocarborane clusters is revealed in photoemission spectra. The exposure of mercury to semiconducting boron carbide leads to increased electrical resistance. These latter results suggest that mercury interacts with the solid films of the dehydrogenated C_2B_{10} icosahedra (semiconducting boron carbide). This interaction is consistent with theory we have undertaken [18] and is different from any expectation that would result from the very weak interaction observed between mercury (Hg) and the molecular (hydrogenated C_2B_{10}) orthocarborane.

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