

July 1992

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Lee, Sunwoo; Li, Dongqi; Cendrowski-Guillaume, Sophie M.; Dowben, Peter A.; Perkins, F. Keith; Frigo, S.P.; and Rosenberg, R.A., "Electronic structure of borane cage molecules adsorbed on Si(111)" (1992). *Peter Dowben Publications*. 141.  
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# Electronic structure of borane cage molecules adsorbed on Si(111)

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(Received 23 October 1991; accepted 16 December 1991)

We compare the valence band photoemission resulting from molecular adsorption of *nido*-decaborane(14) ( $B_{10}H_{14}$ ) and *nido*-2,3-diethyl-2,3-dicarbaheptaborane on Si(111) at 100 K. The relative shift of the apparent valence band edge with increasing molecular coverage is consistent with the relative energy difference in the highest occupied molecular orbital for these two molecules as inferred from modified neglect of differential overlap calculations. The results suggest that the screening is very similar, despite the very different molecular structures of these two *nido* cage molecules.

## I. INTRODUCTION

Recently, a number of photoemission studies of condensed polyhedral cage molecules such as the fullerenes have been undertaken.<sup>1-5</sup> Smaller cage molecules, such as boranes, molecularly adsorbed onto solid surfaces have also been studied via photoemission.<sup>6-8</sup> With increasing interest in the electronic structure of cage molecules molecularly adsorbed onto solid surfaces, the effect of screening upon the electronic structure, as derived by photoemission, is of considerable importance.<sup>1</sup>

We have recently demonstrated that *nido*-decaborane (14), ( $B_{10}H_{14}$ ),<sup>7</sup> and *nido*-2,3-diethyl-2,3-dicarbaheptaborane,  $C_2B_4H_6(C_2H_5)_2$ ,<sup>6,8</sup> can be adsorbed molecularly on Si(111). It is possible to compare condensed molecular films of these two molecules. Both molecules contain ten atoms of carbon and/or boron and a similar number of hydrogens (14 and 16, respectively), and are based upon *nido* cage molecular structure. Nonetheless, despite these similarities in size, the molecular structure of these two cage boranes are very different as seen in Fig. 1. Comparison of condensed films of these two molecules is therefore of particular interest. We compare photoemission results for adsorbed films of these two molecules on Si(111) substrates. Semiconductor substrates, such as silicon, provide weaker screening of the molecular film in photoemission than is the case for metallic substrates. The resulting referencing of the occupied molecular orbitals to the vacuum level should therefore be more pronounced for these semiconductor substrates. This effect will be particularly pronounced at low temperatures when surface conductivity of the substrate is depressed.

## II. EXPERIMENTAL

The *nido*-decaborane(14) was obtained from the U.S. Army at Redstone Arsenal, vacuum sublimed and stored *in vacuo* prior to use. The *nido*-2,3-( $C_2H_5$ )<sub>2</sub>-2,3- $C_2B_4H_6$

(denoted throughout this paper as diethylcarborane) was prepared by literature methods.<sup>9</sup> The identity and purity of the compounds was determined by nuclear magnetic resonance (NMR), infrared (IR), and mass spectral measurements and compared with literature values.<sup>9</sup>

The photoemission experiments with diethylcarborane were undertaken in an angle resolved photoemission system equipped with a hemispherical electron energy analyzer as described in detail elsewhere.<sup>10</sup> All the photoemission spectra were taken with the electrons collected normal to the surface with a light incidence angle of 70° off the surface normal. The photoemission experiments with the decaborane were performed using a spherical sector analyzer as described elsewhere.<sup>11</sup> The photon energy throughout this work was 55 eV. The photoemission experiments were conducted at the Synchrotron Radiation Center in Stoughton, Wisconsin and utilized the 1 GeV (Aladdin) ring. The light was dispersed by either a 3 m or a 6 m toroidal grating monochromator.

The Si(111) substrates were polished and etched prior to insertion into the vacuum systems. The samples were then prepared *in situ* as described previously.<sup>6-8</sup> In addition, lengthy annealing of the samples were also undertaken to 900 °C following repeated flashing of the silicon crystals to 1250 °C. This methodology was found to give a 7×7 reconstruction of the Si(111) surface as well as clear indications of all the Si(111) surface states which have been characterized in detail by photoemission.<sup>12</sup> All pressures reported in this work are uncorrected for ionization gauge cross section. Decaborane was introduced into the ultrahigh vacuum (UHV) system by a gas dosing system directed at the substrate surface. For decaborane the coverages may be taken as absolute assuming unity sticking coefficient. Because of the borane and carborane exposure methodologies, only relative changes in exposure may therefore be compared and reported exposures may not be

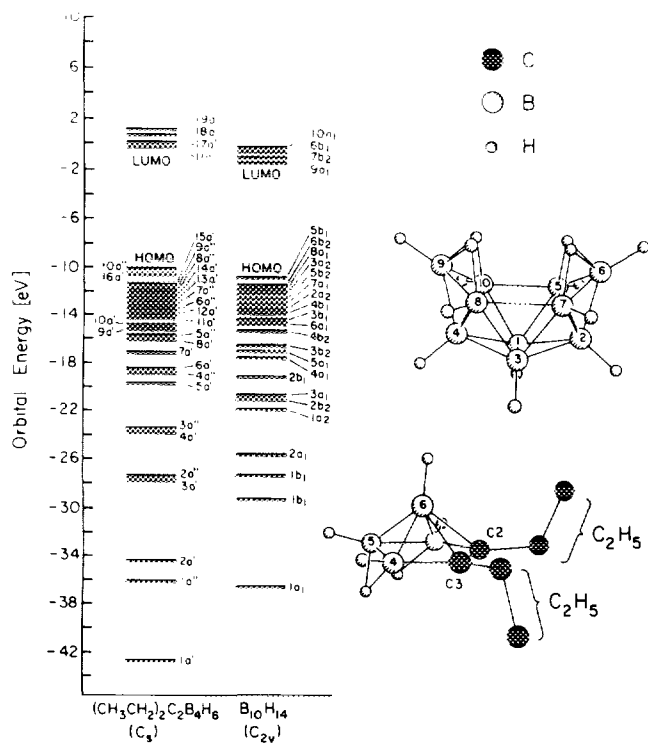


FIG. 1. MNDO calculated minimum energy geometries and molecular orbital energies for nido-decaborane (14) and nido-2,3-( $\text{CH}_3\text{CH}_2$ )<sub>2</sub>-2,3- $\text{C}_2\text{B}_4\text{H}_6$ . The hydrogens on the borane cages and the ethyl groups have been omitted for clarity. The cage numbering scheme is indicated. The results are taken from Refs. 6, 19, and 20.

taken as an indication of absolute molecular film coverages.

### III. RESULTS

From the photoemission spectra taken from the surface following exposure to decaborane (14), as seen in Fig. 2, we concluded that the initial adsorption of decaborane on Si(111) at 100 K is largely molecular. The photoemission spectra exhibit features resemble (Fig. 2) the photoemission features reported for gas phase decaborane.<sup>13-16</sup> The differences between the photoemission spectra of the gaseous species<sup>13,15</sup> and our adsorbed species can be attributed to spectral broadening of the photoemission features frequently observed with many molecular adsorption systems.<sup>17</sup>

Molecular adsorption is also observed with the adsorption of diethylcarborane on Si(111) at 100 K, as seen in Fig. 3 and as reported elsewhere.<sup>6,8</sup> Unlike decaborane, the photoemission spectra following initial exposures of Si(111) to diethylcarborane are substantially different than the photoemission spectra obtained at large exposures as seen in Fig. 3. These differences have been explained by partial dissociation of the diethylcarborane species on the Si(111) substrate at low coverages.<sup>6</sup> This results in the adsorption of oriented  $\text{C}_2\text{B}_4\text{H}_6$  molecular clusters and the loss of the exopolyhedral ethyl groups.<sup>6</sup> Continued exposure of Si(111) at 100 K results in adsorption of molecular diethylcarborane with little or no loss of the exopolyhedral

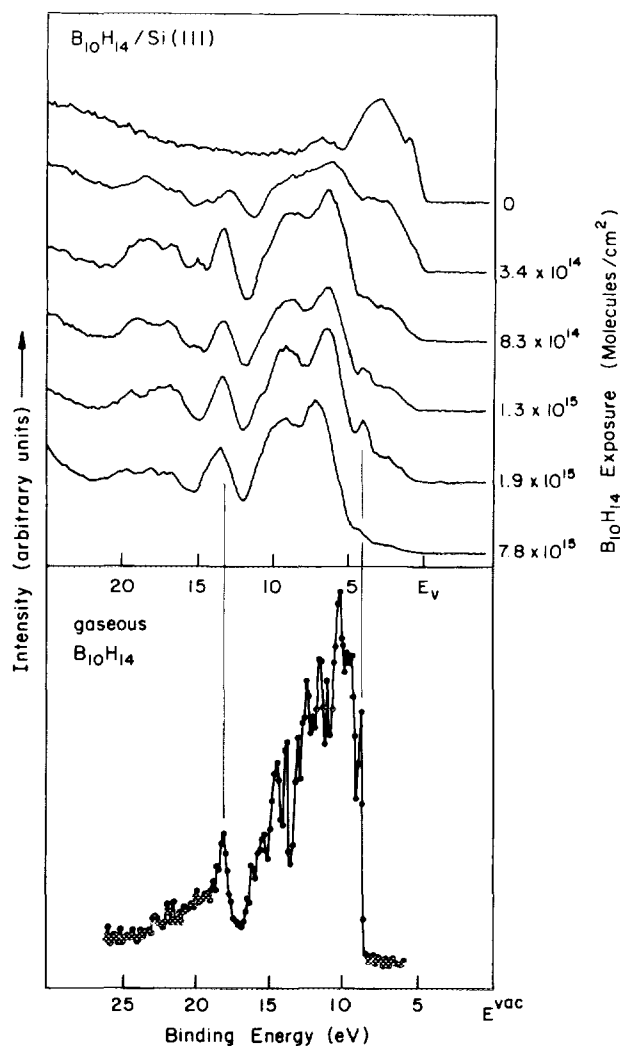


FIG. 2. The photoemission spectra of Si(111) at 100 K with increasing exposure to decaborane. The results are compared with a spectrum of gaseous decaborane. The photon energy is 55 eV.

ethyl groups.<sup>6</sup> From angle resolved measurements it is clear that with increasing molecular adsorption of diethylcarborane, the molecules adsorb with decreasing preferential orientation with respect to the surface normal.<sup>6</sup>

With the molecular adsorption of both diethylcarborane and decaborane there is a shift to lower kinetic energies of the apparent valence band edge as seen in Fig. 4. In other words, using the accepted methodology summarized elsewhere<sup>18</sup> to determine the valence band edge, there is a shift in this cutoff of the occupied states relative to the Fermi energy. For decaborane this shift is  $1.3 \pm 0.1$  eV to lower kinetic energies following exposures of Si(111) to  $85 \times 10^{14}$  molecules/cm<sup>2</sup> or more of decaborane. For diethylcarborane the shift is  $0.45 \pm 0.05$  eV to lower kinetic energies with exposures of 64 L ( $114 \times 10^{14}$  molecules/cm<sup>2</sup>) or more. Based upon the attenuation of the silicon substrate signal in photoemission the apparent valence band edge shift is complete only with molecular coverages greater than at least two molecular monolayers. As discussed below, the differences between the behavior for these two molecules may be attributed not to differ-

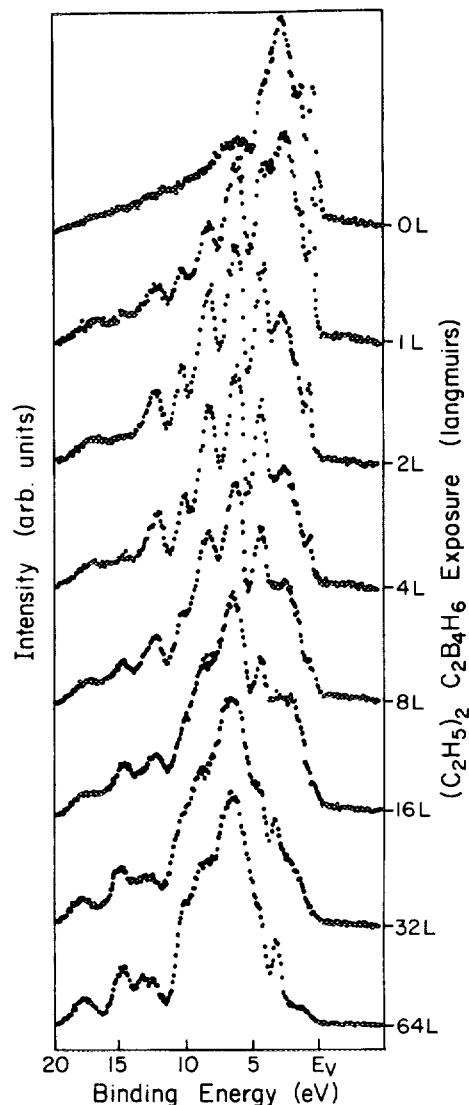


FIG. 3. The photoemission spectra of Si(111) at 100 K with increasing exposure to nido-2,3-( $\text{CH}_3\text{CH}_2$ )<sub>2</sub>-2,3- $\text{C}_2\text{B}_4\text{H}_6$ . All photoelectrons were collected normal to the surface. The photon energy is 55 eV.

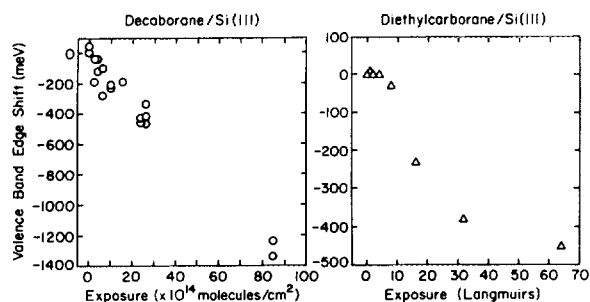


FIG. 4. The shift in relative kinetic energy of the valence band edge for Si(111) at 100 K following exposure to boranes. No significant changes relative to the high coverage data points shown are observed with continued increasing coverage.

ences in physical structure but rather to differences in their molecular electronic structure.

#### IV. DISCUSSION

The molecular orbitals of decaborane<sup>13-15,19</sup> and diethylcarborane<sup>6</sup> have been calculated and are schematically shown in Fig. 1. Using the same semiempirical modified neglect of differential overlap (MNDO) calculated molecular orbitals<sup>20</sup> for diethylcarborane<sup>6,19</sup> and decaborane<sup>19</sup> the relative energy differences between the highest occupied molecular orbitals (HOMO) may be compared. For decaborane, this  $5b_1$  orbital has a calculated energy of 11.29 eV below the vacuum level as compared to 10.97 eV by *ab initio* self-consistent field-molecular orbital (SCF-MO) calculations<sup>14,15</sup> and the experimental ionization potential of 10.15 eV.<sup>15</sup> For diethylcarborane the  $10a''$  orbital is calculated to be some 10.32 eV below the vacuum level by MNDO.<sup>6</sup>

While the calculated binding energies from MNDO cannot be taken as a good indication of the absolute binding energies, the relative differences between the highest occupied molecular orbital for one species as compared to another should be quite accurate.<sup>19,20</sup> For diethylcarborane on Si(111), the energy difference between the binding energies with respect to the clean Si(111) valence band edge and the calculated molecular orbital binding energies is observed to be  $7.3 \pm 0.2$  eV. This energy difference can in part be explained by the work function and substrate screening effects. Thus the most accurate value to be obtained by this theoretical approach is the energy difference between the HOMO of diethylcarborane and the HOMO of decaborane, which is 0.97 eV. It is important to note that photoemission is a final state spectroscopy, while the calculated molecular orbitals are more representative of the initial state. This is readily apparent from the photoemission spectra shown in Figs. 2 and 3. Because of many body final state effects in photoemission,<sup>21,22</sup> the apparent valence band edge is at a greater kinetic energy than the highest occupied molecular orbitals (observed via photoemission) readily assigned on the basis of the MNDO calculations<sup>6-8,19,20</sup> by some 2.4 eV.

Adsorption of these borane cluster molecules on Si(111) should result in only weak screening of the adsorbed molecular species in the photoemission process. If the screening is very weak, then the apparent valence band edge becomes increasingly dominated by the HOMO density of states. If the bonding of the molecular species is weak and lateral and substrate interactions are small, then the HOMO density of states is referenced strongly to the vacuum level as is the case for photoemission of adsorbed xenon (PAX).<sup>23</sup> Thus the energy difference in the apparent valence band edge shift between these two molecules should be dominated by the HOMO binding energy differences. At least this should be the case in the weak screening limit. This picture is certainly consistent with the observation that both decaborane and diethylcarborane are weakly adsorbed on Si(111). Both molecular decaborane<sup>7</sup> and diethylcarborane<sup>8</sup> desorb from Si(111) below room temperature.

For condensed films of these two molecules, on Si(111), the apparent valence band edge shifts differ by 0.85 eV (1.3–0.45 eV) from our results. This is in surprisingly good agreement with the value expected from calculation (0.97 eV). These preliminary results suggest that these two different borane cluster species are screened only very poorly by Si(111) in photoemission for two or more molecular monolayers. Regardless of the extent of the substrate screening for these two molecules, it is clear that the screening of these two molecules, both by the substrate and by adjacent molecules is very similar for the molecular multilayer film.

It is important to note that for the lower molecular coverages, changes in the valence band edge (Fig. 4) cannot be easily compared for the two molecules. Suppression of the surface state,<sup>5</sup> slightly different molecular chemisorption processes,<sup>5</sup> and potential surface doping<sup>6,7</sup> all compete in changing the valence band edge in the low coverage region. Analysis of this valence band edge shift, unlike that for the large coverage limit, cannot be made without further theoretical modeling.

## V. CONCLUSION

The adsorption of molecular decaborane and diethylcarborane is clearly possible on Si(111) at 100 K at large exposures. This is suggested not only by the valence band photoemission results but also by the good agreement between the apparent valence band edge shift difference and the difference between the calculated molecular (HOMO) orbitals. Further studies with other similar molecular clusters, particularly species with radically different molecular orbitals is indicated in order to confirm the postulates proposed here with regard to photoemission screening.

## ACKNOWLEDGMENTS

The authors would like to acknowledge helpful conversations with John Weaver (University of Minnesota) and to thank J. Glass and J. T. Spencer (Syracuse University) and T. A. Whelan (SUNY Potsdam) for their assistance and encouragement particularly in assisting in the creation of Fig. 1. The authors would also like to thank M. Onellion for his considerable technical support. This work was funded by the National Science Foundation (NSF) through Grant No. DMR-88-20779. This work was carried out at the Synchrotron Radiation Center which is funded by the NSF.

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