Adsorption of Lead Phthalocyanine on the Ge(111)-c(2×8) Surface

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The adsorption of lead phthalocyanine on the clean Ge(111) surface has been studied with photoelectron spectroscopy and scanning tunnelling microscopy. A strong interaction of the molecule with the surface has been observed through changes in the Pb 5d and C 1s core levels of the adsorbate, plus the Ge 3d core level of the substrate. This interaction can also reduce Pb from the phthalocyanine macrorcycle from a 2+ to a neutral state. It is demonstrated through STM that this interaction is strongest at defect sites and step edges, and in fact on the unperturbed c(2×8) reconstruction, which dominates the surface, the molecules are seen to be significantly mobile at room temperature. This shows a dramatic passivating effect of this reconstruction when compared with other similar semiconductor surfaces. [DOI: 10.1380/ejssnt.2009.234]

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I. INTRODUCTION

The interfaces between metal phthalocyanines (MPc) and inorganic semiconductors have attracted interest for the purposes of constructing hybrid devices that could integrate conventional semiconductor knowledge with the various possibilities that organic semiconductors present. Phthalocyanines are thermally and chemically stable organic semiconductors making them an attractive option for practical applications.

A number of studies of various MPc and derivatives have been conducted on the Si(111)-(7×7) and Si(001)-2×1 surface [1–6]. Photoelectron spectroscopy shows significant changes in the carbon and nitrogen core levels of adsorbed MPc [1, 2, 4] and substrate auger emission shows changes in surface related features [2], all indicative of a strong interaction between molecule and substrate. Furthermore scanning tunneling microscopy (STM) studies of copper phthalocyanine (CuPc) on Si(111) and Si(001) show individual molecules distributed across the terraces [2, 3]. In the case of Si(001) the molecules are well resolved and show specific adsorption sites suggesting very little mobility of molecules across the surface. Although on Si(111) lateral resolution of the molecules is lost and specific adsorption sites can not be determined, low mobility is still indicated through observation of fixed molecules on terraces. Similar to CuPc on Si(001), MgPc on Ge(001) shows low mobility of the molecules with specific adsorption sites of individual molecules on the terrace [7].

On both the Si(001) and Si(111) surfaces a further effect is possible for some phthalocyanines whereby the central metal ion is reduced. Photoelectron spectroscopy of the Cu 2p core level of CuPc shows a distinct shoulder consistent with Cu being stripped from the molecule on Si(111), but not on Si(001) [1, 2], while studies of F16CuPc show the Cu being removed from the molecule even on on Si(001) [6]. Interestingly, for lead phthalocyanine (PbPc) on Si(111) and Si(001) the reaction is not observed [4]. This is unexpected given that this metal atom is readily removed upon annealing of interface layers [8], and upon deposition on platinum substrates at room temperature [9]. It is possible that the metallic Pb peak in the spectra of ref. [4] is obscured due to poor statistics and the use of a slightly larger film thickness.

This paper presents photoemission and STM results of PbPc deposited on the clean Ge(111) surface, which reconstructs in a c(2×8) pattern as shown in the model in Fig. 1 [10]. Three surface atom types exist: adatoms; first layer atoms bonded to these adatoms; and unsaturated first layer atoms, commonly designated as rest atoms. This reconstruction involves a transfer of negative charge from adatoms to the rest atoms [11]. Photoemission demonstrates a strong interaction between molecule and substrate, similar to studies on Si. Furthermore the Pb is seen to be stripped from the molecule. Despite this, STM shows a distinct passivating effect of the c(2×8) reconstruction such that upon small coverages the molecules accumulate on step edges and defect sites, indicative of a significant mobility of molecules across the terraces.

II. EXPERIMENTAL

All photoemission measurements were conducted at beamline SGM1 at the ASTRID synchrotron facility. The germanium wafer was cleaned in-situ through several cycles of sputtering with 0.5 keV electrons, annealing at 600 °C then gradually cooling the sample. This process was repeated until a crisp c(2×8) LEED was visible, the surface shift of the Ge 3d core level was clear and no carbon was apparent in the photoelectron spectra.

The scanning tunnelling microscopy (STM) experiments were carried out in an Omicron VT UHV-STM system. The same cleaning procedure was used as for the spectroscopy, with surface quality determined by STM imaging.

The PbPc (purchased from Sigma Aldrich) was purified by degassing for a day below sublimation temperature and...
then for three hours at an elevated temperature. It was deposited in-vacuo from a Knudsen-cell at a pressure of approximately $1 \times 10^{-9}$ mbar at a rate of 1 ML per 10 minutes onto a substrate held at room temperature. The film thicknesses were controlled via the use of a quartz crystal microbalance, located at the sample position during calibration then retracted during deposition, and confirmed via the photoelectron core level intensities.

The spectra are decomposed using Voigt profile peaks with a Shirley background. The fitting parameters for the phthalocyanine related peaks at the interface were determined from a thick film where the substrate core levels were entirely obscured.

III. RESULTS AND DISCUSSION

Figure 2 shows the Ge3d core level for progressively increasing coverages of PbPc. The clean spectrum is fitted with four components, following Götzelid et al. [12]. The components in that work were related to: bulk Ge atoms ($\text{Ge}_{\text{Bulk}}$); first layer atoms bonded to the adatoms, at $-0.25$ eV relative to the bulk ($\text{Ge}_{\text{S1}}$); adatoms at $+0.18$ eV ($\text{Ge}_{\text{S2}}$); and rest atoms at $-0.74$ eV ($\text{Ge}_{\text{S3}}$). However, there is reasonable contention from photoelectron holography experiments that the assignment of $\text{Ge}_{\text{S2}}$ and $\text{Ge}_{\text{S3}}$ should be exchanged [13]. A further two components, at lower binding energy than the bulk peak ($\text{Ge}_{\text{I1}}$) and at higher ($\text{Ge}_{\text{I2}}$), are included to deal with interface states generated upon deposition of the PbPc. These extra components should be treated as an indication of where the spectral weight is changing rather than specific, well defined states. However, it is worth noting that no arrangement of the four states employed for the clean surface can account for the adsorbate surface, indicating that new states are induced by the molecule.

From Fig. 2 (and the summary contained in Table I) the most dominant change is in the low binding energy section of the spectrum. The intensity of $\text{Ge}_{\text{S3}}$ is significantly reduced as is the intensity of first layer atoms bonded to the adatoms ($\text{Ge}_{\text{S1}}$), while $\text{Ge}_{\text{S2}}$ remains unchanged. The bulk contribution increases and a significant contribution at $0.48$ eV lower binding energy than the bulk ($\text{Ge}_{\text{I1}}$) is required for a “good” fit. Finally another component ($\text{Ge}_{\text{I2}}$) is included at $0.58$ eV higher binding energy than the bulk peak. This feature is small in comparison to the other peaks. The centre of gravity for the clean Ge 3d spectrum is $-0.13$ eV from the bulk, whereas for the spectrum after 1 ML deposition it is $-0.09$ eV. The transfer of spectral weight from the surface components toward higher binding energy suggests a transfer of electrons from the surface to the molecule.

C 1s photoelectron spectra of a single monolayer of PbPc on Ge(111)-c(2×8) and of bulk PbPc, scaled such that the integrated area of both spectra is the same, are shown in Fig. 3. The bulk spectrum comprises three major features: one at approximately $284.6$ eV, related to carbons in the outer benzene rings; one at $286$ eV, related to carbons in the pyrrole rings as well as a shake-up feature of the benzene carbons; and finally a smaller peak at $287.8$ eV resulting from a shake-up of carbons in the pyrrole ring. Meaningful fitting of the monolayer spectrum is difficult due to the multitude of possible interac-

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FIG. 1: Model of the c(2×8) reconstruction of the Ge(111) surface.

FIG. 2: Ge3d photoelectron spectra of PbPc deposited onto the Ge(111)-c(2×8) surface. Four doublets are used in the fitting of the clean germanium spectrum, with a further two included for interface states.
TABLE I: Summary of fitting parameters used in Fig. 2. The energy difference between the germanium peaks is kept constant. The intensities are given as a fraction of the total intensity. For all peaks a Gaussian FWHM of 0.33 eV, Lorentzian FWHM of 0.15, spin orbit split of 0.59 eV and a branching ratio of 0.66 were used.

|            | Clean | 1/8 ML | 1/2 ML | 1 ML  |
|------------|-------|--------|--------|-------|
| $I_{Ge_{Bulk}}$ | 0.44  | 0.45   | 0.48   | 0.51  |
| $I_{Ge_{21}}$   | 0.32  | 0.31   | 0.23   | 0.19  |
| $I_{Ge_{22}}$   | 0.13  | 0.13   | 0.13   | 0.13  |
| $I_{Ge_{23}}$   | 0.10  | 0.10   | 0.09   | 0.07  |
| $I_{Ge_{11}}$   | 0.00  | 0.00   | 0.04   | 0.07  |
| $I_{Ge_{12}}$   | 0.00  | 0.00   | 0.01   | 0.02  |

![Graph](image-url)

**FIG. 3:** C 1s photoelectron spectra of PbPc deposited on the Ge(111)-c(2×8) surface, taken with a photon energy of 350 eV. Both spectra are scaled such that the integrated area under the curve is the same.

![Graph](image-url)

**FIG. 4:** Pb 5d photoelectron spectra of PbPc deposited onto the Ge(111)-c(2×8) surface. Three doublets are used in the fitting of the spectrum, two related to Pb in the phthalocyanine, attributed to Pb above the molecular plane (Pb$_{11}$) and Pb below the molecular plane (Pb$_{12}$), and one related to lead stripped from the molecular macrocycle Pb$_{13}$.

resulting from the large ionic radius of the Pb ion it protrudes to one side of the molecular plane. The two peaks can therefore be attributed to molecules where the Pb is pointing towards the substrate surface and away from the substrate surface, as seen in the case of PbPc or SnPc deposited on Ge(001)-2×1 [14]. This then raises the question of which peak is associated with which geometry.

The main possible mechanisms for such energy shifts at interfaces are charge transfer or final state screening. Given that the Ge 3d core level show a shift of intensity to higher binding energy, indicative of electron transfer from the surface to the molecule, a charge transfer shift to lower binding energy of the molecule core level would be expected. Likewise, final state screening effects are expected to cause a shift to lower binding energy. On this basis it is reasonable to assign the lower binding energy peak of the phthalocyanine (Pb$_{12}$) to the molecules with the Pb towards the Ge surface. Conversely Pb$_{11}$ is assigned to molecules with the Pb protruding away from the Ge surface.

The lowest binding energy peak (Pb$_{13}$) occurs at 18.3 eV, consistent with Pb atoms in a neutral (metallic) state, as opposed to the +2 state of Pb ions in the molecule. The FWHM of this peak is 0.55 eV, compared to 0.85 eV for the Pb5d core level of the lead phthalocyanine, again consistent with metallic lead seen in ref. [9]. This is clear
Reexamining the PES in light of the STM it appears that the reaction which reduces the Pb is probably only able to occur at defect sites. For small coverages a large fraction of molecules will be fixed on the reactive defect sites seen in the STM, as the coverage increases the proportion of signal from these sites will decrease. From Table II it is clear that the proportion of Pb 5d signal arising from metallic Pb decreases with increasing coverage. Between the $\frac{1}{8}$ ML and $\frac{1}{4}$ ML coverages there is still an increase in the intensity of the metallic Pb signal (although the proportion of the overall signal is lower), but to within the experimental accuracy there is no further increase for the 1 ML coverage. This agrees with the expectations of the metal being reduced only at defects and further demonstrates the passivating effect of the c(2×8) reconstruction.

A final point, raised as a potential subject of future work, comes from an examination of the intensities of the various Pb 5d core level components. In each case Pb$_{12}$ (attributed to PbPc where the Pb is towards the substrate surface) represents a fixed contribution of the overall intensity (approximately 50%), the remainder divides between Pb$_{11}$ and Pb$_{13}$. Furthermore, when the sample with 1ML PbPc coverage was heated to 100 °C for two hours peak Pb$_{11}$ (Pb away from the substrate) decreased and Pb$_{13}$ (metallic Pb) increased correspondingly, while Pb$_{12}$ remained constant. This suggests the observed reaction is a transition between the Pb$_{11}$ and Pb$_{13}$ states. Perhaps counterintuitively, this suggests that it is molecules with the Pb away from the surface that are able to react. This could provide an interesting insight to the mechanism by which the ion is removed from the macromolecule.

### IV. CONCLUSION

A strong interaction between the adsorbed PbPc molecules and the Ge(111) surface is demonstrated through photoelectron spectroscopy. This includes a reduction of the Pb from the PbPc molecule. However, it is shown through the use of STM that the molecules are significantly mobile over the c(2×8) reconstruction on the terraces, being locked in at defect sites and domain boundaries. This shows a dramatic passivating effect on the surface of this reconstruction when compared with the Ge(001)-2×1, Si(111)-7×7 and Si(001)-2×1 surfaces where the molecules are adsorbed equally on terraces and steps.

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**Table II: Summary of fitting parameters used in Fig. 4.** The energy difference between peak Pb$_{11}$ and peaks Pb$_{12}$ and Pb$_{13}$ is constant at -0.65 eV and -1.83 eV respectively. GW refers to the Gaussian FWHM, LW the Lorentzian FWHM, SOS the spin orbit split and BR the branching ratio. The intensities are given as a fraction of the total intensity.

|            | 1/8 ML | 1/2 ML | 1 ML |
|------------|--------|--------|------|
| I$_{Pb_{11}}$ | 0.21   | 0.29   | 0.37 |
| I$_{Pb_{12}}$ | 0.50   | 0.53   | 0.53 |
| I$_{Pb_{13}}$ | 0.29   | 0.18   | 0.10 |

| Pb in PbPc | Pb in metal |
|------------|-------------|
| GW         | 0.70 0.46   |
| LW         | 0.26 0.17   |
| SOS (eV)   | 2.64 2.64   |
| BR         | 0.75 0.75   |

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**Figure 5:** Filled state STM images of a submonolayer coverage of PbPc on Ge(111): (a) an 80×80 nm image of steps on the surface; (b) A 45×45 nm image of a terrace with three different rotational domains (labelled B, C and D) of the c(2×8) reconstruction.

Evidence that Pb is stripped from some molecules upon deposition, as seen in PbPc deposited on Pt(111) [9]. In Fig. 5(a) a filled state image of steps on the Ge(111) surface with a submonolayer coverage of PbPc is shown. Although the lateral resolution of the molecules is very poor, as seen on Si(111) [2], it is clear that molecules cluster along step edges. Figure 5(b) shows a filled state STM image of a terrace containing three different rotational domains of the c(2×8) reconstruction (labelled B, C and D). In this case it is the boundaries between the different rotational domains that have picked up the molecules, while the areas where the reconstruction is undisturbed display no adsorbed molecules. It should be noted that the point marked A in Fig. 5(a) where a cluster of molecules appears has several different rotational domains of the reconstruction, and is not an accumulation of PbPc on a c(2×8) terrace. These results provide an interesting contrast with STM work conducted on MPC on Ge(001)-2×1 where the molecules were seen to adsorb with distinct sites across the dimer reconstructed terraces of the surface [7]. They indicate significant mobility of molecules across the c(2×8) reconstruction, and a marked increase in interaction wherever this reconstruction is disturbed.

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