Scanning Tunneling Microscopy Observation of
Germapericyclicine on a Graphite Surface*

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Room temperature scanning tunneling microscopy (STM) has been carried out on two newly synthesized organic molecules, octabutylgerma-4-pericyclicine C₈H₇Ge₄ and dodecaphenylgerma-6-pericyclicine C₆H₁₆Ge₆, at atmospheric pressure condition. A regular array of cluster-like patterns and square patterns are observed for C₈H₇Ge₄ molecules. Straight lines structures of regular periodicity of about 5.5 nm are noticed for C₆H₁₆Ge₆ molecule. Some molecular islands are also observed for both molecules by STM. Therefore the molecules tend to self-assemble on the graphite surface. Spectra obtained from X-ray Photoelectron Spectroscopy (XPS) and X-ray Fluorescence Spectroscopy (XFS) support the molecular assembly on the substrate surface even in an ultra high vacuum condition.

1. Introduction

Recently the structure and the functionality of organic molecules on a surface have attracted much attention from the viewpoint of their potential applications to organic light emitting devices, various sensors, and versatile molecular and biological recognitions. For these reasons, a monolayer film on an inert surface supports a suitable model system for studying the 2 or 3-dimensoinal molecular phenomena. Scanning Tunneling Microscopy (STM) provides the means to observe the structures and dynamics at solid-solid or solid-liquid interfaces in atomic-scale. So, if it is possible to make an ordered array of a new molecule on a substrate surface, the new molecule's functionality could be increased because the energy transfer from the molecule to the surface become effective through the same effective path.

The newly synthesized Germapericyclicines are denoted as "Ge-4-Bu" for octabutylgerma-4-pericyclicine [nBu₂Ge(C=Ge)]₄ where 'Bu' means the butyl group -C₈H₁₇ and "Ge-6-Ph" for dodecaphenylgerma-6-pericyclicine [Ph₆Ge(C=Ge)]₆ where 'Ph' stands for the phenyl group -C₈H₅ in this study. Ge-4-Bu molecule is in a liquid phase at room temperature with a molecular weight 843.44 C₈H₁₇Ge₄ and Ge-6-Ph molecule is in a fine crystalline state with a molecular weight 1505.04 C₆H₁₆Ge₆. So, in this paper we will present some investigations on these two organic molecular films. Fig. 1 shows the structures of both molecules. Fig. 1(a) and (c) show single molecular structures and Fig. 1(b) and (d) show the grouped molecular structures for the molecules Ge-4-Bu and Ge-6-Ph, respectively. In Fig. 1(a) the inside four Ge (Germanium) atoms are connected like a square in the Ge-4-Bu molecules and the estimated bonding distance between Ge-Ge atoms is 0.485 nm. The estimated diameter of the molecule is about 1 nm. In the case of Ge-6-Ph molecule in the Fig. 1(c), inner six Ge atoms are bonded with each other in a hexagonal frame and the bonding distance from the top Ge atom to the bottom Ge atom is about 0.913 nm. So the diameter of the single molecule is more than 1 nm including the bonding distance of the outer phenyl group.

Highly Oriented Pyrolytic Graphite (HOPG) is selected as a suitable substrate for its properties of large-scale atomically flat terraces, chemical inertness and easy cleavability to observe the above-mentioned unknown molecules on it. In this paper HOPG will be denoted simply as graphite.

It is well known to STM researchers that the thermal diffusions of the molecule, versatile floor vibrations, various noises etc. are the major obstacles in observing the real organic molecular structure on an inert surface at room temperature by STM observation. Even in such circumstances, we obtained some images of molecular array at room temperature atmospheric conditions.

Our aim in this study is to create an ordered array of the molecules on the graphite surface so that we can measure the structures of the molecules by stereo atomscope⁸ to understand a basic phenomenon for the various potential applications of organic molecule films.

2. Experiments

The molecules were synthesized and purified in K. Kakiuchi laboratory in NAIST. Due to new molecules it was unknown to us which method would be suitable for these molecules to be adsorptive on a substrate. Here we adopted two methods for the adsorption of the present molecules on the graphite surfaces. In the UHV system, a pulse jet valve (PJV, Parker Hannifin, series-99) was used to deposit the molecules on the substrate surface. During preparing the sample by the PJV, the background pressure was about 6 × 10⁻⁷ Pa. Another adsorption method was a dropping method. In this method the organic molecule was deposited by dropping a droplet on
Fig. 1 Molecular structures (a) single molecule and (b) four molecules of Germa-4-pericyclic; (c) Single molecule and (d) seven molecules of Germa-6-pericyclic.

3. Results and Discussion

Fig. 2(a) and (b) show the SEM images of surfaces obtained from the molecules Ge-6-Ph and Ge-4-Bu respectively by the dropping method. There are some nano-sized holes in Fig. 2(a). We can say that the film is not monolayer as the nano-holes still appeared under the first layer of the film. In Fig. 2(b) by considering pure molecule, the film looks thick. So in both cases, a molecular film is thicker than 1 ML. Fig. 2(c) is a SEM image for the Ge-4-Bu surface adsorbed by PJV method. It would be worth mentioning that in this sample pulse duration was (60 × 500 μs). In this figure, although the amount is different from the dropping method, the molecular film seems lighter than that of Fig. 2(b) and probably one brighter layer on the top of a dark layer is visible. We observed from other SEM sample that the dark layer under the top layer is similar to those obtained from the fresh graphite surfaces. So the PJV method may provide a thinner film than that made by dropping method according to our visual observation on SEM images.

In the room temperature STM observation, both PJV and dropping methods were applied. In the UHV condition, the PJV-adsorbed surface could not as yet provide atomic scale resolution for both molecules by the STM investigation, except some molecular islands. The STM images presented here, all are observed at room temperature atmospheric condition by dropping method. After observing the graphite atomic images in the graphite region on the sample surface as a standard of calibration, the adsorbed region was investigated. Fig. 3(a) and (b) show STM images obtained from the Ge-4-Bu adsorbed surfaces where the tunneling current I is 0.50 nA.
and the sample bias voltage $V_s$ is $+0.09 \text{ V}$. Fig. 3(a) of scanning size $1500 \times 1500 \text{ nm}^2$ shows some molecular islands especially it seems the islands are formed near the graphite step regions. In Fig. 3(b), a regular array was observed in the Ge-4-Bu molecular region. This array extended even across the graphite step region and covered more than $1000 \times 1000 \text{ nm}^2$ area in the original images. The distance between two bright protrusions is 5 nm and this size is larger than the size of a single Ge-4-Bu molecule, hence this pattern is called a "cluster-like pattern" in this paper. The formation of this molecular layer is similar to other organic molecules on the alkane buffer layer reported by Xu et al.\(^{21}\). They also used HOPG as a substrate, but for stability of the molecules they used alkane as a buffer layer between the molecule and the substrate HOPG. It is said that a pattern called 'Moiré pattern' is observed usually in a valley between two steps on a clean graphite surface. The lattices of Moiré patterns are stretched due to small disorientations of the top layer relative to the underlying graphite single crystal lattices\(^{35}\) or due to the simultaneous imaging of the double tip in the vicinity of a grain boundary\(^{40}\). But in our case, the patterns are observed only in the molecular region and cross over several graphite steps area. We observed some differences in the protrusion height parallel to the scanning direction in the layers of cluster structure of Ge-4-Bu molecules. In the Fig. 3(b), the featureless area is attributed to the bare graphite surface and possibly covered with mobile adsorbate that could not be resolved\(^{39}\). Both boundaries of the cluster layer are showing sharp, bright and different structures where the difference in protrusions is between 1.5 nm to 2.5 nm. Some discontinuous cluster lattices are also observed in the upper region of the cluster patterns. From the cross sectional line profile analysis, inter-corrugations height difference is about 0.3 nm in this discontinuous cluster patterns i.e. the corrugations height in the right side is 0.3 nm lower than that of the left side. Liu et al. reported that they were able to observe a bilayer structure of octa-alkoxyl-substituted phthalocyanine (PcOC8) molecule on an HOPG surface in constant current mode observation and the height between two layers was 0.2 nm\(^{39}\). But in our case, this is constant height mode of STM and inter-corrugations heights difference in the discontinuous cluster structures is noticed toward the directions of the tip scanning over the surfaces. Another almost square patterns were observed in
another area on the surface for the molecule Ge-4-Bu, as shown in Fig. 4. In these patterns, the distance between protrusions is about 0.5 nm, which is the same size as that of the single molecule. Fig. 5 shows the STM image obtained from the Ge-6-Ph molecular surface where the accumulation is different from upper half part to lower half of the image. The distance between two lines corrugations is about 5.5 nm, which is larger than the size of a single molecule. In this image although the resolution is poor but we could observe these line patterns by changing scan direction, scan speed, scan size and we have found that the image is relative images of the adsorbed surface. These lines patterns may be yielded from the grouping of the molecules.

We tested RHEED for the molecule Ge-6-Ph. The usual straight lines patterns of graphite lattices were observed from the graphite region by RHEED observation. Some spots and defused ring patterns were observed for the Ge-6-Ph sample prepared by the dropping method. The patterns suggest that the spots were formed from some of small crystals of the molecule.

Fig. 6 shows the x-ray photoelectron spectra obtained from XPS examination for both molecules. In Fig. 6(a), Ge 3d peak is not clear but two steep peaks for C 1s and O 1s from the Ge-6-Ph molecule region are noticed. Fig. 6(b) is a narrow scan spectrum for the molecule Ge-4-Bu where the Ge 3d peak is visible around 30 eV. Fig. 7 shows the fluorescence spectra obtained from both molecules simultaneously by using 15 keV electron excitations. In this figure, two sharp peaks are characteristic x-ray of Ge Kα and Ge Kβ. For both XPS and XFS spectra, some chemical shiftings were observed compared to the pure Ge spectra.

4. Conclusion

Two adsorption methods were adopted for the understanding of the new adsorbates on graphite surfaces. Some nano-sized holes were observed in SEM images by dropping method for Ge-6-Ph molecule. A clear and regularly assembled cluster-like Ge-4-Bu molecular array with 5 nm periods was observed by STM at room temperature atmospheric condition by the dropping adsorption method. Square like patterns of 0.5 nm period-
licity from the same molecule shows the possibility of obtaining the single molecular atomic structure in future investigations. For the molecule Ge–6–Ph, the line patterns of about 5.5 nm periodicity is a definite evidence for getting the molecular information in the near future by STM. It is still unclear that which adsorption method is better suited for the molecules under investigation. The two patterns (cluster-like patterns and single molecular patterns) obtained from the molecules indicate the possibility to obtain 1 ML film as well as the multilayer film. And it seems the formation of the molecular film depends on the molecular properties, substrate-molecule interactions and the density of the molecule to be adsorbed on the substrate. Besides these facts, the graphite straight-line patterns, some single crystal spots and rings of the molecule were also observed by RHEED. The Ge 3d peaks were observed in XPS and proved the presence of the molecules, even in the UHV condition. XFS also supports the presence of each element for both molecules by their sharp peaks in spectra.

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References