Extended Abstracts of the 2001 International Conference on Solid State Devices and Materials, Tokyo, 2001, pp. 644–645

F-9-1 (Invited)

Electron Tunneling Devices Using Organic Ultra-Thin Films and Specific Dielectric Property of Organic Monolayers

Mitsumasa Iwamoto

Tokyo Institute of Technology, Department of Physical Electronics
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan
Phone:+81-3-5734-2191 Fax:+81-3-5734-2191 E-mail: iwamoto@pe.titech.ac.jp

1. Introduction

Many investigations have been carried out to build up tunnel junctions and molecular rectifying junctions using organic thin films, with the hope of observing novel and useful electrical and optical properties. One example is the exciting idea of unimolecular rectification using a D^{+}-π-A^{-} system by Aviram and Ratner [1], with which many new organic materials have been synthesized and numerous experiments have been done towards the realization of molecular electronics [2]. Electron tunneling rectifier junctions based on electron tunneling via molecular energy states such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) states also calls attention to the novel electronic devices. So far, rectifying properties of junctions fabricated by double-layered organic molecular films have been reported [3]. The author also succeeded in preparing Josephson junctions using polyimide (PI) Langmuir-Blodgett (LB) films as tunneling spacer[4]. Further, the Au/PI/rhodamine-dendorimer/PI/Au (or Al) junctions were prepared using PI film as a tunneling barrier [5], and the I-V characteristic was shown to be very similar to the Coulomb staircase.

Furthermore, the specific property of organic monolayer film calls much attention to electronics application. For example, organic monolayers on the surface have spontaneous polarization due to the so-called symmetry breaking of the monolayer structure. As a result, optical second harmonics (SH) light and Maxwell displacement current can be easily generated [6]. These phenomena are very important in electronics, and find various ways in electronics.

For the last ten years, we have been studying organic monolayers from the viewpoint of dielectric physics, and applying them to electron devices. In this paper, the author summarizes his recent research topics on electron tunneling devices using polyimide Langmuir-Blodgett (LB) films, and discusses the importance of the study of organic monolayer films from viewpoint of dielectric physics.

2. Tunneling Devices using PI LB films

One of the most important application is to use organic thin films as a tunneling barrier. Thus there has been a growing interest in the preparation method of high-quality organic ultra-thin films. Unfortunately, it is still not an easy task to fabricate tunneling junctions using such organic thin films prepared, owing to the presence of pinholes in films themselves and the difficulty in the deposition of top electrodes onto the films prepared without destroying their textures. Fortunately, during the last ten years, the preparation techniques have greatly advanced and various new organic materials have been synthesized. Polyimide (PI) LB films were successfully prepared with a monolayer thickness of 0.4 nm [7]. PI LB films are almost pinhole-free, and thermally and chemically stable up to a temperature of 400 ℃. The PI films show the excellent electrical insulating property, and work as a good tunneling barrier in tunnel junctions such as Josephson Junctions. For example, the current-voltage (I-V) characteristic of Au/PI/Pb-Bi (30%) junctions shows a nonlinear dependence, and the energy gap Δ/e observed in the I-V characteristic changes in a manner as predicted by Bardeen-Cooper-Schrieffer (BCS) theory. The Nb/Au/PI/Pb-Bi junctions show a typical I-V characteristic of SIS Josephson junction [4] and they are very effective in the detection of microwaves. That is, the normal step structure ruled by the Josephson frequency condition $V=nhf/2e$ ($n=1,2,3...$) is clearly seen in the I-V characteristic at a temperature of 4.2 K in the presence of microwaves, where f is the applied microwave frequency and h is the Planck constant. It was suggested that the Josephson junction using PI LB film as tunneling spacer is able to detect microwaves with a high frequency, e.g. 0.5 *THz*.

3. Single electron Tunneling devices Using polyimide LB films

Another important research field using organic thin films as a tunneling barrier is to build up molecular rectifying junctions, electron resonance tunneling device [8], and single electron tunneling (SET) devices. For this purpose, one must prepare well-defined structures incorporating almost pinhole free ultra-thin films possessing functionalized molecules between two metals. Using a two-layer system consisting of phthalocyanine and perylene derivatives, novel electronic molecular diodes have been created on the basis of the asymmetric tunneling through molecular state [3]. The control the electron transfer via molecular energy states becomes crucially important. As the first step, it is essential to investigate the electron transport mechanism via functionalized molecules in artificially arranged multilayer films. Using PI LB films containing porphyrin (PORPI), the electron tunneling current due to the excitation of electronic transition in molecular states of porphyrins has been revealed at a temperature of 4.2 K [9]. Similar experiments were carried out for junctions with a rhodamine-dendorimer monolayer sandwiched between PI LB films. It has been revealed that a step structure is created in the I-V characteristic. The I-V structure is very similar to that seen in so-called Coulomb staircase, and the possibility of single electron tunneling process via rhodamine molecule has been suggested [5, 10].

4. Interfacial and electrostatic phenomena in ultrathin films

In order to clarify the electron injection and transport mechanism in organic monoalyers, the research from the viewpoint of dielectrics is very helpful, because the specific electrical and optical properties of films can be explored in association with the symmetry breaking. The study on the electrostatic interfacial phenomena occurring at the metal/film interface is obviously important before we make junctions using organic thin films, because the information on the energy diagram of devices is absolutely important for the improvement of device performance. To use ultra-thin films whose thickness is less than the electrostatic double layer is helpful. LB films are suitable, because they are prepared onto solid substrates by the layer-by-layer deposition with an order of monolayer thickness. Using the surface potential measurement, the distribution of space charge and the electronic density of states have been determined. The presence of electron-acceptor and donor states has been revealed, and the presence of excessive electronic charges transferred from metals into LB films have been discovered. That is, it was found that very high density of electronic states with an order of 10^{25} -10^{26} m^{-3} and very high electric field with an order of 10^{8} – 10^{9} V/m exist in the interfacial space charge layer within the range of an order of several nano-meters. We then could show that these interfacial phenomena give directly effect upon the electrical transport properties of tunneling devices using PI LB films.

4. Conclusion

Electron tunneling devices such as Josephson junctions and SET devices were prepared using polyimide LB films. For a better understanding of the device operation, the interfacial electrostatic phenomena have been revealed.

Acknowledgments

The author would like to express sincere thanks to the staff of Nano-technology section of Kansai Advanced Research Center, Communication Laboratory under their able Chief, Dr. Shinro Mashiko for insightful discussion. The thanks are also given to the staffs, researchers, and students, who one engaged in their researches and studies in Iwamoto's laboratory. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

References

[1] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277 (1974).

[2] K. Kaneto, K. Kudo, Y. Ohmori, M. Onoda and M. Iwamoto, IEICE Trans. Electron. **E81-C**, 1009 (1998).

[3] C. M. Fischer, M. Burghard, S. Roth and K. v. Klitzing, Appl. Phys. Lett. **26**, 3331 (1995).

[4] T.Kubota, M.Iwamoto, H.Noshiro, andM.Sekine, Jpn.J.Appl.Phys. **30**, L393 (1991).

[5] Y. Noguchi, Y. Majima, M. Iwamoto, T. Kubota, T. Nakahama, S. Yokoyama and S. Mashiko, IEICE Trans., E83-C, 1076 (2000).

[6] M.Iwamoto and C.X.Wu, *The physical properties of organic monolayers*, World Scientific, Singapore, (2001).

[7] M.Iwamoto and M.Kakimoto, *"Polyimides as Langmuir-Blodgett films"*, in *Polyimides, Fundamentals and Applications,* ed. M.K.Ghosh and K.L.Mittal, Marcel Dekker, Inc., New York, (1996). Chapt.25.

[8] W.Schutt, H.Koster, and G.Zuther, Thin Solid Films **31**, 275 (1976).

[9] M.Iwamoto, M.Wada and T.Kubota, Thin Solid Films 244, 472 (1994).

[10] Y. Noguchi, Y. majima and M. Iwamoto, J.Appl. Phys., in press (2001).

[11] E. Itoh and M. Iwamoto, J. Appl. Phys. 81, 1790 (1997).