論文の内容の要旨

論文題目 Fabrication and Physical Properties of Amorphous Superlattices

(アモルファス超格子の作製と物性)

氏　名　栁瀬　隆

1. Introduction

This dissertation deals with new materials composed of superlattices. *Superlattice* is a periodic structure of layers of two or more different materials. Figure 1 shows the schematic illustration of superlattice composed of two components. In the early stage of the research on superlattice, epitaxial grown III-V compound semiconductors such as GaAs/AlAs have been mainly investigated. However, it is difficult to deposit more than several hundred layers because deposition rate is very small. In next stage, inorganic amorphous semiconductor, especially Si-based superlattices, have been investigated due to the large deposition rate. However, there are still disadvantages such as high defect density near interfaces and low electric performance.

Fig. 1: Superlattice composed of two components

In recent studies, many kinds of organic amorphous materials have been developed in the research of organic light emitting diodes, solar cells, polymer actuators, and so on. There is no disadvantage that inorganic materials have for organic materials. Therefore, it has been considered that these materials open up a new opportunity for fabricating macroscopic materials with the nano-scale multilayer as designed.

A final goal in this study is the development of photo-switching piezoelectric material. Photo-switching piezoelectricity is piezoelectricity that can be induced by light irradiation, not by electric field application. To develop the photo-switching piezoelectric materials, it is necessary to combine the concepts of the photovoltaic effect and the piezoelectric effect. Tri-color superlattice (three-component superlattice) (TCS) is one of the most realistic candidates to fabricate the photo-switching piezoelectric materials because the photovoltaic and piezoelectric effect can be achieved by selection of appropriate materials. p-type and n-type semiconductor (p-n junction) are needed for photovoltaic effect. Insulator is needed for piezoelectric effect.

2. Experimental

A new fully-automated apparatus has been developed for fabricating amorphous superlattices (Fig. 2). It utilized an optical heating for the rapid deposition and a QCM for precise thickness control. The sample was rotated to guarantee the in-plane uniformity of the superlattice films. The deposition sequence and thickness of each layer could be set by only inputting parameters to fabricate superlattices as designed. In order to complete one layer, 20 sec was typically required. Therefore, a superlattice with more than hundreds layers could be prepared in almost one day.

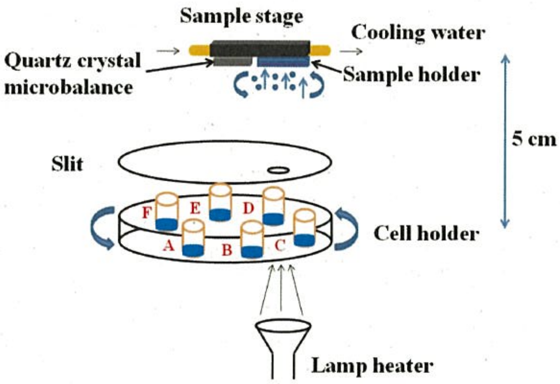

Fig. 2: Automated deposition apparatus for fabricating amorphous superlattices

Amorphous materials used in this study were N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (NPB) tris(8-hydroxyquinolinato) aluminum (Alq_3), molybdenum oxide (MoO_3), and polyurea (PU). NPB is a p-type semiconductor and Alq_3 is an n-type semiconductor. NPB and Alq_3 are used in organic light emitting diodes as a hole transport layer and a electron transport layer, respectively. MoO_3 is a wide gap semiconductor (mostly insulator) and used for a charge separation layer in mechanically flexible solar cells. PU is a piezoelectric insulator and can be fabricated by vacuum deposition polymerization without by-products.

First, Alq_3/NPB superlattice was fabricated in order to confirm the machine performance. X-ray diffraction (XRD) pattern derived from superlattice was observed and the surface morphology was smooth by AFM observations. These results indicated the developed apparatus worked as designed.

Next, PU films were prepared by alternating deposition of DAF (diamine) and MBCI (diisocyanate), and then I investigated its physical properties. Indium tin oxide (ITO) substrates and Si substrates with thermal oxide layer (700 nm) and aluminum layer (200 nm) (Al/SiO_2/Si) were used for suitable characterization technique. IR spectroscopy was carried out to investigate the degree of the polymerization and piezoelectric measurement was done by mechanical stress application method and capacitance method.

TCS films composed of Alq_3, MoO_3 and NPB (Alq_3/MoO_3/NPB) were prepared on the Si substrates. XRD and AFM measurements were carried out to investigate the smoothness of the interfaces and the uniformity of thickness. Photovoltage measurements were also carried out, which is very important to develop the photo-switching piezoelectric materials.

PU/NPB/Alq_3 films were prepared by the sequence of $((DAF - MBCI)_m - NPB - Alq_3)_n$. The morphology of the surface was estimated by AFM observations. Photovoltaic measurement was carried out, and then the photo-switching piezoelectricity was measured by capacitance method.

3. Results and discussion

3-1 Physical properties of PU films

It was found that PU can be synthesized by alternating deposition although the conditions of the supply ratio (DAF:MBCI) to achieve particle-free and flat PU films was very severe. Judging from the reaction scheme, the ratio of DAF to MBCI should be exactly 1:1. If the ratio is appropriate, the surface of PU films is free from particles and the film is optically transparent. Otherwise the surface of PU films becomes white with particles. Furthermore, the surface of PU films fabricated by alternating deposition was smooth by AFM observations.

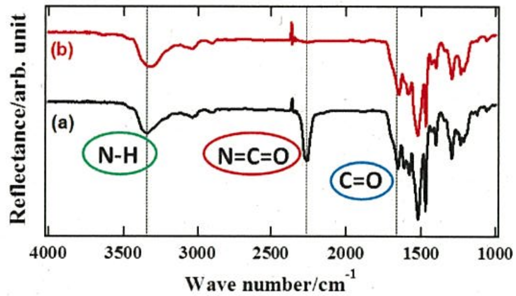

Fig. 3: IR spectra

(a) as-deposited, (b) after thermal treatment

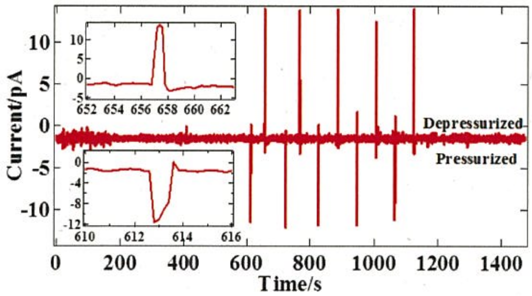

Fig. 4: Current signals when mechanical stresses were applied

The degree of polymerization, which is a very important factor for application as a piezoelectric material, was investigated by IR spectroscopy as shown in Fig. 3. The absorption peak at around 2270 cm^{-1} formed by stretching vibration of isocyanate group was observed for (a) as-deposited sample although the peak disappeared (b) after thermal treatment. This result indicates that remained isocyanate group further copolymerize with amino group by thermal treatment.

Figure 4 shows the piezoelectric response obtained as current signals when mechanical stresses were applied and released to the poled PU films. It indicates that PU films fabricated by alternating deposition show the piezoelectric property by the poling treatment and that PU could be used as a component of TCSs for fabricating the photo-switching piezoelectric materials. Capacitance method also indicated the poled PU film has the piezoelectricity and piezoelectric constant calculated from this method was 2.6 pC/N. This value is smaller than the reported value of aromatic polyurea, which may be attributed to larger molecular weight.

3-2 $Alq_3/MoO_3/NPB$ superlattice

X-ray diffraction (XRD) measurement was carried out and diffraction peak originating from TCS of $Alq_3/MoO_3/NPB$ were observed. This result indicates interfaces of $Alq_3/MoO_3/NPB$ were smooth and thickness of each layer could be controlled. Root-mean-square roughness obtained by AFM observation was around 0.50 nm, which also indicates the interfaces of $Alq_3/MoO_3/NPB_3$ were smooth. A 100-multilayer sample showed a photovoltage of more than 10 V.

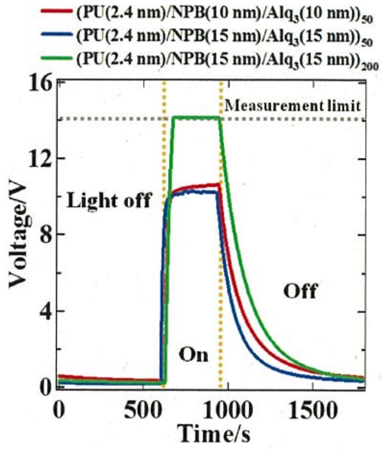

Fig. 5: Photovoltage of $PU/NPB/Alq_3$

3-3 Photo-switching piezoelectricity of $PU/NPB/Alq_3$

The surface morphology of the $PU/NPB/Alq_3$ films was examined by AFM as a function of repetition time. The surface of $PU/NPB/Alq_3$ films was relatively smooth despite the films were relatively thick. Furthermore, large photovoltage was observed if PU layer in $PU/NPB/Alq_3$ superlattice was thick. Figure 5 shows the results of photovoltaic measurement on three kinds of $PU/NPB/Alq_3$. Maximum voltage was more than 14.1V that is the limitation of the measurement when $(PU(2.4\ nm)/NPB(15\ nm)/Alq_3(15\ nm))_{200}$. Figure 6(a) shows the photo-switching piezoelectric measurement by capacitance method. The effect of thermal expansion was comparable to the piezoelectric effect. Then, a difference between TCSs poled by forward and reverse bias was calculated (Fig. 6(b)). This capacitance change induced by light irradiation clearly shows the photo-switching piezoelectric effect.

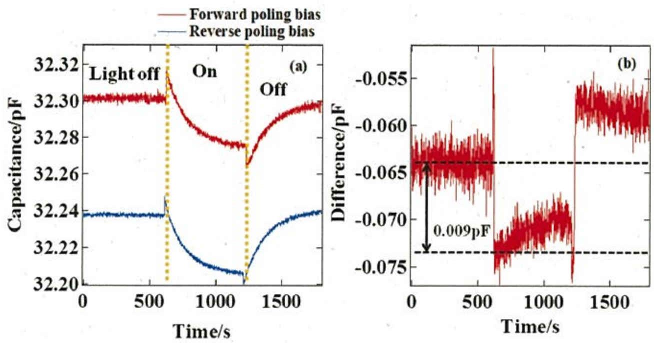

Fig. 6: Photo-switching piezoelectric measurement by capacitance method

4. Conclusions

An apparatus specially designed to fabricate amorphous superlattices with more than hundred layers was developed. Piezoelectric PU was prepared with nm-thickness control by alternating deposition. Fabrication of TCSs of $Alq_3/MoO_3/NPB$ and $PU/NPB/Alq_3$ was succeeded and large photovoltage was observed. The photo-switching piezoelectricity was observed for $PU/NPB/Alq_3$ superlattice by capacitance method.