Extended Abstracts of the 1991 International Conference on Solid State Devices and Materials, Yokohama, 1991, pp. 393-395

# Invited

# Integrated Optoelectronic Devices Based on Organic/Inorganic Heterojunctions

## S. R. FORREST and F. F. SO

Departments of Electrical Engineering and Materials Science National Center for Integrated Photonic Technology University of Southern California Los Angeles, CA 90089-0241

A new class of engineered materials based on organic semiconductors vacuum deposited onto the surfaces of inorganic semiconductor substrates is described. Based on these novel heterojunctions, novel devices such as photodetectors, field effect transistors and waveguides have been demonstrated. In this paper, the growth, fabrication, and characterization of these devices is given in detail. We also discuss the conditions which lead to ordered growth between lattice mismatched organic thin films into novel "quasi-epitaxial" structures such as fully organic multiple quantum wells. The interesting linear and nonlinear optical properties of these structures are also considered.

#### 1. Introduction

Recent work in many laboratories worldwide [1-4] has demonstrated a new class of engineered materials with application to photonic devices. These materials are variously known as "van der Waals solids", "layered materials" or "quasi-epitaxial materials". The property which these materials have in common is that the cohesive force which bonds the various material layers together is the relatively weak van der Waals force. This results in the ability to layer materials which are highly lattice-mismatched without inducing defects in the crystal structure. One particularly interesting class of van der Waals solids with applications to a very broad range of optical and electronic devices is based on structures consisting of crystalline organic semiconductors [1]. These materials have been found to have excellent electrical and optical characteristics when grown by the ultrahigh vacuum process of organic molecular beam deposition (OMBD) onto other organic semiconductors, or even onto the surfaces of inorganic semiconductors such as Si, GaAs or InP [5]. For example, high bandwidth photodetectors consisting of layers of perylene-based compounds deposited on Si substrates have been demonstrated [6], as have field effect transistors based on organic/InP heterojunctions [7]. Furthermore, waveguides and other optical devices have been demonstrated using these quasi-epitaxially grown layers [8]. However, before a family of devices can be realized which is practical for use in demanding photonic systems applications, it is important that issues surrounding process compatibility with other semicon-ductors, and environmental stability of the constituent materials is proven. In this paper, we will discuss several novel devices based on organic semiconductors, and on the organic/inorganic semiconductor heterojunction (OI-HJ). Device fabrication and performance details will be discussed, and evidence that the OI-HJ is in fact a very electrically stable junction in a wide variety of environments will also be presented. Taken together, our results indicate that novel heterojunction optoelectronic devices based on crystalline organic materials may provide a new class of practical devices for advanced photonic systems.

#### 2.Active Optoelectronic Devices

We have found that many crystalline organic materials, and in particular those based on the archetype compound, 3,4,9, 10 perylenetetracarboxylic dianhydride (PTCDA) form rectifying heterojunctions when deposited onto the surfaces of inorganic semiconductor substrates. This heterojunction is the basis of a large variety of active electronic devices which we have demonstrated for use in optoelectronics. The basic heterojunction structure is shown in Fig. 1. Typically < 1000 Å of the organic material is deposited by vacuum



sublimation onto a precleaned and deoxidized semiconductor surface. Prior to deposition it is important to purify the organic source material. Typically, this can be achieved using either successive gradient sublimation of the commercially available crystalline material, or alternatively by refluxing in a high boiling point solvent. The highest purity is obtained using the former technique. The semiconductor can be either p or n-type, and can be chosen from a wide variety of group IV, III-V or II-VI compounds such as Si, Ge, GaAs, InP, CdTe, etc. The junction between the organic film and the semiconductor substrate is the heterojunction which ultimately determines the properties of the device. Next, ohmic contacts are deposited onto the exposed substrate surface as well as onto the organic material. For PTCDA, typical ohmic contact materials include indium, tin, titanium, and indium-tin-oxide (ITO). Currentblocking contacts to PTCDA are obtained using gold or aluminum.

Due to the very large anisotropies in the conductivity of the organic thin film, the applied electric field (and hence the current in the device) is confined only to the region beneath the contact pad. That is, there appears to be no lateral spread of the current, hence making the device fabrication extremely simple, since no device isolation other than that determined by the extent of the contact, needs to be employed.

Typical bipolar current-voltage (I-V) characteristics of an In/PTCDA/p-Si device are shown in the inset of Fig. 2 [9]. Here, the substrate free carrier concentration was 3 x  $10^{15}$  cm<sup>-3</sup>. From these characteristics, it is observed that the forward current increases exponentially with voltage, whereas the reverse I-V characteristics show avalanche breakdown at -150V. We attribute reverse breakdown to avalanche in the Si substrate. A detail of the reverse I-V characteristic is shown in Fig.2. For a diode area of  $1.25 \times 10^{-4}$  cm<sup>2</sup>, it is apparent that the dark current at 50V is ~1 nA, which in this case is probably limited by generation and recombination within the Si substrate.

Such devices have obvious uses as avalanche photodetectors, since the OI-HJ can be used to apply large voltages across the underlying substrate. Due to the uniformity of the electric field under the contact pad, it is possible to make such photodiodes with both high quantum efficiency and avalanche gain [6]. This has indeed been demonstrated in our laboratory, where gains approaching 100 have been observed. In addition, the low leakage current OI-HJ can be used in many other depletion mode devices such as field effect transistors [7].

It is useful to estimate the ultimate bandwidth to be expected from such depletion mode devices. In previous work, it was found that ITO/PTCDA/p-Si photodiodes with a 1500 Å thick organic layer had a rise/fall time limited by transit of carriers across the PTCDA of 5 ns [6]. This implies a carrier (hole) velocity of 3000 cm/s. We have demonstrated that it is



possible to deposit continuous thin films of  $\leq 50$  Å, giving an ultimate switching time of ~150 ps. In fact, as the growth technology improves and the layer thicknesses are reduced, even shorter device time constants are to be expected. Nevertheless, 150 ps time constants implies a bandwidth of f = 1 GHz, which is adequate for many important optoelectronic applications.

#### 3. Patterning and passivation

Another important question to be answered regarding the practicality of the OI-HJ for use in systems applications is related to the physical and electronic stability of the devices. We have successfully developed means for photolithographically patterning and passivating OI-HJ devices, and have demonstrated longterm stability in their electrical characteristics [9].

In Fig. 3 is shown a schematic cross-section of a patterned OI-HJ device. After deposition of the organic thin film, a 3000 Å thick layer of SiO<sub>2</sub> is pyrolytically deposited at 150°C using a mixture of silane and oxygen. This acts as a "patterning" layer onto which photoresist can be deposited and patterned without damaging the softer crystalline organic layer, and also prevents contaminants from diffusing through the organic thin film to the OI interface.



To pattern the devices, a negative photoresist is spun onto the SiO<sub>2</sub> surface, and then is patterned using standard techniques. Next, this pattern is "duplicated" in the SiO<sub>2</sub> by etching using 10:1 H<sub>2</sub>O:HF, which does not attack the PTCDA film. Next, ohmic metallization is deposited (typically Ti/Pt/Au), and contacts are defined by once again patterning the wafer surface, and then etching away those regions not contacting the PTCDA layer.

We have tested the environmental stability of such devices using In as the top contact, and the results of long term measurements of the dark current of the diodes held at elevated temperature is shown in Fig. 4. For the first 1000 hr., the diodes were held at 80°C and the dark currents were measured periodically at room temperature. It is observed that, although the dark current of some of the diodes was as low as 300 pA, there was no degradation of the devices over this time period. After 1000 hr., the temperature was increased to  $100^{\circ}$ C (limited by the softening temperature of the In contact). After 3000 hr. total aging time, only one device was observed to fail, as indicated by a dark current increasing from < 1 pA to 2 pA over a period of 2000 hr.



Although these tests are a very preliminary indication of the stability of the devices, it appears that indeed the OI-HJ can form the basis of a reliable device technology for use in advanced optoelectronic systems.

# 4.Devices based on quasi-epitaxial organic growth

We have demonstrated that crystalline organic molecules can, under some conditions, be deposited in a crystalline form on many substrates even though the films are highly lattice mismatched with the substrate. This unusual, ordered form of growth is termed "quasiepitaxy" (q-e). The charge transport and optical properties of these novel layered structures provide an unusually large range of possibilities for materials and device physicists. In effect, their combination of physical properties bridge the materials spectrum between semiconductors and insulators, and opens the prospect for a broad new class of engineered materials for use in future generation optoelectronic device applications. To summarize our findings to date, q-e crystalline organic compounds have several properties which, taken together, make them unique in the known spectrum of materials:

1. Many crystalline materials bonded by vdW forces can be grown into ordered q-e films on substrates or other films without regard to lattice matching requirements.

2. The anisotropic crystalline structure of the films results in giant anisotropies in their conductive and dielectric properties. As an example, PTCDA films have a

birefringence of  $\Delta n = 0.66$ . Recently, polarizationselective waveguides employing the large birefringence of PTCDA have been demonstrated [8].

3. Heterojunctions consisting of two organic films in contact with each other often exhibit electrical and optical properties analogous in many ways to fully inorganic heterojunctions [10].

4. Evidence for quantum confinement in very thin layer organic multiple quantum well structures has furthered our understanding of the nature of excitons in crystalline organic materials. In addition, the observation of quantum confinement suggests that many devices based on organic MQWs are becoming a realistic possibility. One example of such a device would be an organic MQW optical modulator which could be made to cover all regions of the UV, visible or near IR spectral regions, depending on the choice of organic compounds employed.

### 5. References

1. F. F. So, S. R. Forrest, Y. Q. Shi and W. H. Steier, Appl. Phys. Lett., <u>56</u>(1990) 674.

2. S. R. Forrest, M. L. Kaplan and P. H. Schmidt, J. Appl. Phys., <u>56</u>(1984) 543.

3. M. Hara, H. Sasabe, A. Yamada, and A. F. Garito, Japan. J. Appl. Phys., <u>28</u>(1989) L306.

4. K. Ueno, K. Saiki, T. Shimada and A. Koma, J. Vac. Sci. Technol., <u>A8</u>(1990) 68.

5. S. R. Forrest, M. L. Kaplan and P. H. Schmidt, Ann. Rev. Mat. Sci., <u>17</u>(1987) 189.

6. F. F. So and S. R. Forrest, IEEE Trans. Electron. Dev., <u>36</u> (1988) 66.

7. C.-L. Cheng, S. R. Forrest, M. L. Kaplan, P. H. Schmidt and B. Tell, Appl. Phys. Lett., <u>47</u>(1985) 1217.

8. D. Y. Zang, F. F. So and S. R. Forrest, Appl. Phys. Lett. <u>59</u>(1991).

9. V. Prabhakar, S. R. Forrest, J. P. Lorenzo and K. Vaccaro, IEEE Photonics Technol. Lett., <u>2</u>(1990) 724.

10. F. F. So and S. R. Forrest, Phys. Rev. Lett., <u>66</u>(1991) 2649.