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# Influence of modified surface of gaas on properties of heterostructures with organic semiconductors

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Mol. Cryst. Liq. Cryst., Vol. 384, pp. 49–54 Copyright © 2002 Taylor & Francis 1058-725X/02 \$12.00 + .00 DOI: 10.1080/10587250290112917 OR & FRA LOIS

### INFLUENCE OF MODIFIED SURFACE OF GaAs ON PROPERTIES OF HETEROSTRUCTURES WITH ORGANIC SEMICONDUCTORS

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The electrical, optical and photoelectric properties of organic/inorganic semiconductors heterostructures are investigated depending upon the interface microrelief morphology modified by chemical etching of GaAs. Polishing and anisotropic etchants were used to change it from flat to microtextured (quasigrating-type). The p/n-heterostructures were fabricated by the vacuum evaporation of thin ( $\sim 50\, n$ m) pentacene or phthalocyanine of lead films on modified surface of n-GaAs crystals. A considerable decrease of the optical reflectance and increase of the photosensitivity by a few (1.5–4) times have been obtained for microtextured heterostructures with respect to the flat ones

The results emphasize the importance of GaAs surface chemical microtexturing to future developments of the photocells, based on organic semiconductor/GaAs heterojunction.

Keywords: organic-inorganic heterostructure; photoelectric properties; photosensitivity

#### INTRODUCTION

Applications of thin organic films in organic/inorganic heterostructures (HS) allows to reduce the surface recombination velocity S and to increase a photovoltage  $V_{\rm ph}$ . Last is stipulated by absence of dangling bonds on a surface of organic semiconductors (OS) and consequently on the interface of organic and inorganic semiconductors there are no additional surface electron states, which behave as centers of capture and recombination of non-equilibrium carriers of a charge [1]. However, deposition of organic films on a surface of inorganic semiconductors (IS) does not reduce the

concentration of initially existing surface states. Therefore observable decrease of S value may be insignificant because in the most cases OS are deposited on so-called real surface of inorganic semiconductors with large concentration of initial surface electron states. To modify the OS/IS interface properties the development of method of IS surface microtexturing by chemical anisotropic etching is of considerable interest. These investigations are very important for the enhancement of photosensitivity of surface-barrier heterostructures by means of increasing the utilization of incident light due to reduction in reflection losses and to possible improvement of electronic structure of this micro/nano-relief interface. The last effect is a right consequence of the chemical anisotropic etching of a surface of an inorganic semiconductor single crystal. Besides, these investigations are very interesting from point of view of the organic/inorganic semiconductor interfaces formation, especially their electronic structure.

The goal of the paper is using the technology of anisotropic etching to fabricate microrelief surfaces of III-V semiconductors with improved electronic characteristics [2] for following formation of the interface with organic photosensitive films and the investigation of the influence of the IS surface modifying on the electronic structure, the potential barrier formation, and the photovoltaic effect at the interface.

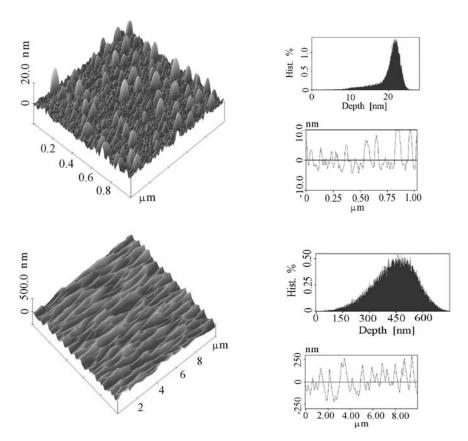
#### **INVESTIGATED STRUCTURES**

n-GaAs plates of (100) orientation with doping concentration  $N_d=2.7\times 10^{16}\,{\rm cm^{-3}}$  have been used for manufacturing heterostructures with organic semiconductors. The surface treatment included chemical polishing (to obtain flat interface) or anisotropic etching surface in 2HF:  $2{\rm H_2SO_4}$ :  $1{\rm H_2O_2}$  solution (to obtain interface microrelief of quasigrating-type morphology) with subsequent etching out of surface oxide layers.

The photosensitive OS films of p-type — pentacene (Pn) (or lead phthalocyanine PbPc) have been deposited by the vacuum evaporation through the mask with circular holes (of 4 mm diameter) on modified GaAs substrates at  $300 \, \text{K}$  temperature. The thickness of OS films was chosen close to the optimal one for Pn ( $\sim 50 \, \text{nm}$ ) [1]).

The semitransparent gold film (with thickness of about 18 nm) has been evaporated in vacuum on the top of OS at room temperature of substrates to obtain ohmic contact with them. For the comparison the gold film was evaporated simultaneously on the same GaAs substrates to make Schottky diodes.

AFM images of surface microrelief of investigated structures and the examples of their section analysis and microrelief height (depth) distribution (bearing analysis) are shown in Figure 1.



**FIGURE 1** AFM images (left) for Au/GaAs structures with flat (a) and textured interface with microrelief of quasigrating type (b), z = 20 (a), 500 (b) nm/div. On the right-histograms of the depth distribution (bearing) analysis and microrelief height distribution (section analysis).

#### EXPERIMENTAL RESULTS

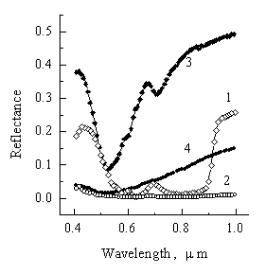
The measurements have shown that photoresponse of the investigated structures at low level of irradiation  $(10^{13}-10^{14}\,\mathrm{quanta/cm^2})$  is rather stable and reproducible. Characteristics of Au/Pn/GaAs structures retain invariable also under simulated AMO solar irradiation, while some degrading of parameters of Au/PbPc/GaAs structures has been revealed under solar irraditiation. Therefore, the results of investigation for Pn/GaAs structures will be mainly presented in this paper.

The experimental spectral reflectance (R) spectra, measured at near normal incidence of light, for the structures Pn/GaAs and Au/Pn/GaAs are

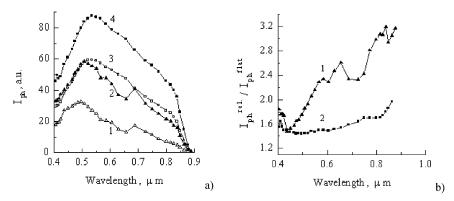
shown in Figure 2. It is seen that the Au film increases the R values considerably though remains some spectral peculiarities *typical* for Pn/GaAs structures. In the same time the interface microrelief causes a significant decrease of R and smoothing its spectral characteristic both for Pn/GaAs and Au/Pn/GaAs structures.

Spectra of the short-circuit photocurrent, density normalized to a constant number of the incident light quanta,  $I_{\rm ph}$  for the investigated structures are presented in Figure 3(a). The spectral dependencies of the coefficient of  $I_{\rm ph}$  increasing due to textured interface (the ratio of Iph for textured interface to Iph for the flat one) for the same structures are shown in Figure 3(b). It is seen from spectral characteristic, that  $I_{\rm ph}$  is mainly caused by the photogeneration of current carriers in GaAs substrate though the peculiarities of its spectrum depend on the OS film optical properties (correlation of  $R_{\rm min}$  with  $I_{\rm ph}$  max). The same peculiarities manifest themselves also in the  $I_{\rm ph}^{\rm rel}/I_{\rm ph}^{\rm flat}$  spectra. So, one of the main cause of the  $I_{\rm ph}^{\rm rel}/I_{\rm ph}^{\rm flat}$  enhancement for Au/Pn/GaAs structures is the increase of light transmittance into GaAs substrate due to the change of optical properties of structures, in particular as a result of the decrease of R value.

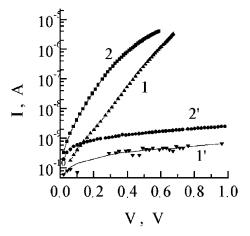
The dark I—V characteristics for Au/Pn/GaAs structure with flat and textural interface are shown in Figure 4. It is seen that both the flat and textured OS/GaAs interfaces have rectifying barrier properties. The non-ideality parameters of direct I—V curves change from 2.4 for the flat



**FIGURE 2** The reflectance spectra of pentacene (Pn)/GaAs (1,2) and Au/Pn/GaAs (3,4) structures with flat (1,3) and microtextured (2,4) interfaces with a surface microrelief of quasigrating type.



**FIGURE 3** (a) The spectral dependences of the short-circuit photocurrent density, normalized to o constant number of incident light quanta,  $I_{ph}$  for Au/Pn/GaAs (1,2) and Au/GaAs (3,4) heterostructures with flat (1,3) and microrelief (2,4) interface. (b). The spectral dependences of the ratio of Iph for textured interface to Iph for the flat one for Au/Pn/GaAs (1) and Au/GaAs (2) heterostructures.



**FIGURE 4** The dark forward (1,2) and reverse (1',2') I–V characteristics of Au/Pn/GaAs heterostructures with flat (1,1') and microrelief (2,2') interface.

structure to roughly 1.85 for textured one. The barrier height for the flat structure was evaluated to be  $\sim 0.9\,\mathrm{eV}$  assuming above barrier injection of charge carriers as dominating mechanism of the current transfer. So, both the photocurrent spectra and dark I–V characteristics testify that the native surface states of GaAs are remained on their interface with OS and determine the diffusion potential in the interface space charge region of GaAs. The last may be concluded also from the comparison of light I–V

characteristics of structures measured under simulated AM0 illumination. The open-circuit voltages of Au/GaAs and Au/Pn/GaAs structures are practically equal (Voc  $\cong 0,60\,\mathrm{V}$  for Au/GaAs and 0,59 V for Au/Pn/GaAs). But the great series resistance of the last (~6 k $\Omega$  for the textured structure and (~9 k $\Omega$  for the flat one) decreases the short-circuit current and fill factor and thus conversion efficiency, of OS/GaAs structures.

The photosensitivity of investigated Au/OS/GaAs heterostructures is seen to increase considerably due to microtexturation of interface, and this enhancement is greater compared to the case of Au/GaAs Schottky diodes (Figure 3b). The increased short-circuit photocurrent density of textured Au/Pn/GaAs structure was obtained to yield increase by a factor of 3.4 in AMO power conversion efficiency.

#### CONCLUSIONS

A considerable decrease of the optical reflectance and increase of the photosensitivity by a few (1.5–4) times have been found for microtextured organic semiconductor/GaAs heterostructures with respect to the flat ones. The results emphasize the importance of GaAs surface chemical microtexturing to future developments of the photocells in particular solar cells, based on organic semiconductor/GaAs heterojunction.

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