УДК 548.4:548.734

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ELECTROCHEMICAL DEFECT CHARACTERIZATION OF DIFFERENT COMPOUND SEMICONDUCTOR SURFACES

У роботі наведено результати досліджень розподілу дефектів у різних напівпровідникових сполуках (GaAs, InGaAs та InP) за допомогою селективного електрохімічного травлення. Отримано картини розподілу дефектів у поперечному та вертикальному напрямках. Для селективного анодного розпаду в різних поляризаційних умовах застосовано сім різних типів електролітів. Досліджено морфологію електрохімічно травленої поверхні за допомогою електронного скануючого і оптичного мікроскопів та поверхневого голкового профілювання. Проведено порівняння одержаних результатів з результатами *X*-променевої топографії та теоретичними моделями.

In this paper, the defect distribution in different compound semiconductor materials (GaAs, InGaAs and InP) is investigated by selective electrochemical etching. Defect maps are obtained both in lateral and vertical directions. Seven different electrolytes were applied under different polarization conditions for the selective anodic dissolution. The electrochemical etched surface morphologies were investigated by scanning electron and optical microscopy and surface stylus profiling. The results were compared to those of *X*-ray topography and theoretical models.

Introduction

One of the most important parameters in semiconductor technology is the density and spatial distribution of the disorders and defects in bulk and epitaxial crystals. There are several widely used methods to examine crystal defects. For example, their lateral distribution can be investigated by selective chemical etching; another commonly used method is *X*-ray topography (XRT). The depth distribution can be studied by transmission electron microscopy.

Selective electrochemical dislocation development is a relatively simple and quick method. Its bears none of the disadvantages of the other methods: it is a fast method with good resolution, the set-up is simple, and the etching parameters can be varied continuously. By this method, the defect distribution can be investigated in both lateral and vertical directions. The method relies on the formation of a transparent Schottky-like contact at the electrolyte-semiconductor interface. Various electrochemical processes can take place at such interfaces. After electrochemical etching the surface generally remains structured; the roughness of the remaining surface depends on many factors, namely, the applied reverse bias, etching current, intensity of the illumination, the material system used, the density of defects and the thickness of the removed layer. Practically smooth remaining surface is required for most of the measurement techniques [1]. Under special etching conditions the morphology of the etched surface is characteristic of the defect density of the surface.

In this work we present results of selective electrochemical etching obtained on three different compound semiconductor materials: GaAs, InGaAs and InP. We study the effect of electrolyte material and the polarization conditions and etch current, and show examples of lateral and vertical defect maps.

Experimental technique

The arrangement of our electrochemical measuring set-up is often used in electrochemical investigations. The working electrode is the semiconductor sample, the counter electrode is made of carbon and the reference electrode is a saturated calomel electrode. The bias voltage source is a potentiostat (Radelkis OH-405). The measurement is controlled through an IEC bus interface by a microcomputer [2]. The thickness of the removed layer is determined by Faraday's law and surface-stylus profiling.

Ohmic contacts to the samples were made using alloyed Sn dots and current leads fixed with silver paste. Samples were mounted in the electrochemical cell either with a sealing ring, or on a metallic sample holder with non-pertinent parts of the surface being

coated with resistive varnish and immersed into the electrolyte. The following electrolytes were used for the anodic etching: (i) 0,1M Tiron metal indicator ($C_6H_4Na_2O_8S_2$), (ii) 10% KOH, (iii) 0,5M HCl, (iv) 36% HCl: methanol (1:99), (v) 36% HCl: 70% HNO_3: methanol (36:24:1000), (vi) 10% NH_4OH, (vii) 5% H_2SO_4.

The morphologies of the etched surfaces were studied by scanning electron microscopy (SEM) and the etch pit density (EPD) values determined on the surface area of about 1 mm^2.

Lateral Dislocation Map Development in GaAs epitaxial structures

GaAs epitaxial structures, grown by chloride transport vapor phase epitaxy were used for the measurements [3]. The substrate was *n*-type, (001) oriented. Before epitaxial growth, an in situ etching was performed in the reactor tube to remove the damaged surface layer. The carrier concentration in the layers was about $1{,}2\cdot10^{17}$ cm^{-3}. For electrochemical investigations, electrolytes (i), (ii) and (iii) were used. The measurements were done in two different polarizing ranges.

In the first set of experiments, the anodic dissolution was carried out by very small polarization: bias voltage being from –0,2 to 0 V. Holes, which are necessary for oxidation, were generated by optical illumination. The wavelength of the illuminating light corresponds to the band gap of the semiconductor. The etch current was kept at a low value, the current density was less than $2\cdot10^{-4}$ A/cm^2. This value remained constant until the end of the process. Easily perceptible etch pits were obtained after removing about 2 μm layer. Typical pits are shown in Fig. 1. The EPD was $2{,}3\cdot10^3$ cm^{-2}.

Next, the anodic dissolution was carried out at a large polarization and in darkness. The holes were generated on the surface by inversion without applying illumination. In this case the etch current increased continuously during the etching process. Typical etch pits are shown in Fig. 2. The EPD was about $2\cdot10^4$ cm^{-2}.

The electrochemical experiments at low polarization were compared with XRT studies, performed before the electrochemical dislocation development. The XRT investigations were done with a double crystal diffractometer using CuK_α-radiation. The surface morphology investigated with both methods on the same area where the dislocation maps show good agreement [4].

In the case of low polarization all three experimental parameters (voltage, current and light intensity) have small values. We therefore suppose that at low light intensity, the atoms of the lowest binding energy are dissolved first, so dissolution takes place mainly at the dislocations. This way dislocation can be developed. On the other hand, in the case of large polarization the holes required for etching are generated by inversion at the surface. The inversion at the crystal imperfections is significantly greater than at other places, thus, in these places the etching process is stronger. Current filaments develop along the defects so the etch pits are crater-like (see Fig. 2.).

Fig. 1. Typical SEM picture of the etch pits in *n*-GaAs; EPD=$2\cdot10^3$ cm^{-2}. Experimental conditions: electrolyte (ii), bias voltage 0 V, etch current $1{,}8\cdot10^{-4}$ A/cm^2.

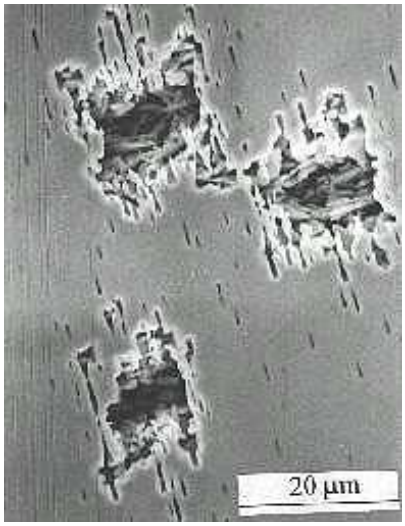

Fig 2. Typical SEM picture of etch pits in *n*-GaAs, dark etching; EPD = $2\cdot10^3$ cm^{-2}. Experimental conditions: electrolyte (iii), bias voltage 2,2 V, etch current is increased during the process.

Dislocation Depth Profiling in InGaAs/GaAs

In these experiments, the threading defects were looked at in $In_xGa_{1-x}As/GaAs$ heterostructures grown by molecular beam epitaxy (MBE). The substrate is p-type and (001) oriented. The specified EPD of the substrate is less than $5 \cdot 10^4 cm^{-2}$. Prior to growth the surface was bombarded by 30-mA Ar^+ ion beam to remove the damaged layer. Then a GaAs buffer layer was grown to improve the morphology of surface, followed by the $In_xGa_{1-x}As$ layer which varied in composition from sample to sample. The layer composition, the growth mode and growth rate were controlled by direct Faraday-cup detected reflection high energy electron diffraction oscillations [5]. We investigated two samples: (A) layer thickness h=1,2μm and composition x=0,3; (B) layer thickness – 3,2 μm and composition – 0,03. The lattice mismatch is f= =0,024 and 0,0024, respectively. This layer is much thicker than the critical layer thickness (CLT) for the generation of misfit dislocations [6]. The calculated CLT is about 8 nm and 800 nm for samples (A) and (B), respectively.

For this study, electrolytes (iii), (vi) and (vii) were tried. After etching, the surface is well structured when larger than 0,5 V anodic bias applied. We carried out the defect etching at about 0,6 V bias, where the current density was less than $2 \cdot 10^{-3} A/cm^2$.

Typical SEM pictures of the surface morphology of samples (A) and (B) are shown in Fig. 3.a and b. The measured EPD of the substrate was half of the value specified by the supplier. The size of etch pits are different; larger pits indicate dislocations traveling further from the interface; this is an indirect evidence for the depth inhomogeneity of the defect density. The elongated shape of the pits due to the higher etch rate along one of the <011> axes.

Several theoretical models have been worked out to predict the threading dislocation density in mismatched heteroepitaxial system. Ayer's equilibrium glide model appears to be the closest to the physical base [7]. The measured EPD values versus etched depth are shown in Fig. 4., together with those predicted by the model.

The difference between the model and our measurements is striking, however the overall h and f dependence agrees well. This discrepancy may have several reasons. It has been reported that EPD measurements tend to underestimate the real dislocation density. Another possible effect may stem from the depth dependence of the dislocation density: the dislocations that terminate close to the actual etched surface may yield pits that are too small to be observed. Thus, we have to shift the EPD points by at least 0,5 μm in our curve [8]. The main cause is, however, probably due to the limitations of the equilibrium glide model [9]. The model assumes that initially there is enough number of threading dislocations in

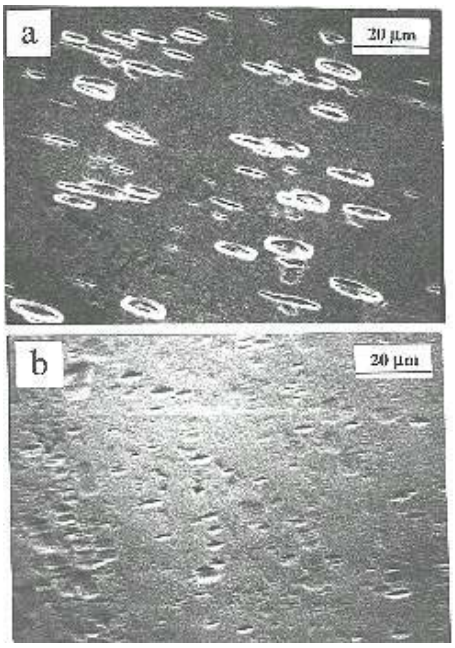

Fig. 3. SEM micrographs of the etched surfaces of InGaAs, (a) sample (A), at 0,7 μm from the interface, EPD is about $2 \cdot 10^8$ cm^{-2}; (b) sample (B) at 0,9 μm from the interface, EPD is about 10^7 cm^{-2}.

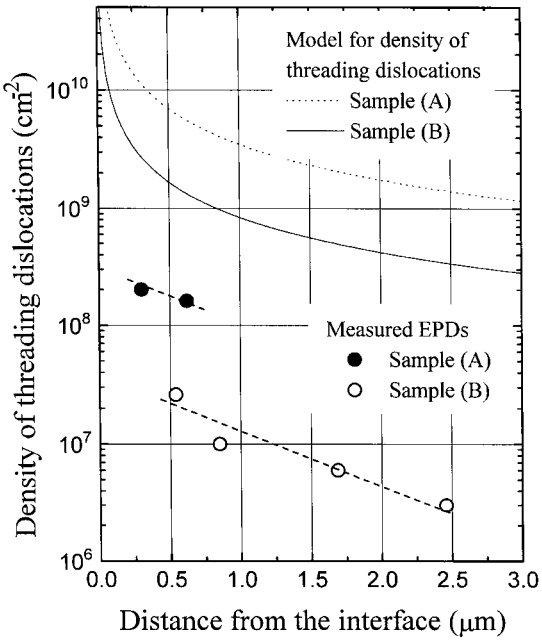

Fig. 4. EPD as the function of etched depth for the InGaAs samples, together with model calculations. The lines serve only as guides to the eye.

the system. Thus, if the number of the threading dislocations is limited, what is typical in small-misfit systems, the threading dislocation density might be smaller than the equilibrium one. In addition, increasing of the annihilation rate due to the in-plane anisotropy may further decrease the threading dislocation density.

Surface Morphology in the Non-selective Polarization Range

At a bias chosen at the plateau of the I-V characteristic, the surface remains slightly structured, too. To demonstrate this feature, *n*-type, (001) oriented GaAs and InP substrates were used. Three kinds of HCl based aqueous electrolytes: (iii), (iv) and (v) recommended in particular for InP were used. The etching gave a sufficiently smooth surface for GaAs if the bias voltage was chosen on the plateau of the polarization curve. With decreasing HCl content of the electrolyte, the surface of the GaAs became increasingly smoother. For InP, we found an opposite behavior: the surface remained smooth even at the highest HCl content. After layer removal, the GaAs surface contained macroscopic etch pits, and the morphology showed fractal behavior with fractal dimension of 1,60. In contrary, for InP the contrast structure of SEM picture fills up the whole etched surface, showing no fractal behavior [10].

Conclusion

Electrochemical etching is an effective and feasible tool to develop crystal imperfections (mainly dislocations) in compound semiconductors. The results show good agreement with *X*-ray topography on the same area. We have shown that selective electrochemical etching is suitable not only for obtaining lateral dislocation maps but also for depth-dependent study of defect density in lattice- mismatched heteroepitaxial systems. In the nonselective etching range, the surface still remains slightly structured. This morphology shows, in certain cases, fractal behavior.

Acknowledgments

This work was supported by the Hungarian Scientific Research Fund (OTKA) through Grant No.T030426 and T020596. This work was presented at the Third International Conference on Physical Problems in Material Science of Semiconductors (September 7-11, 1999, Chernivtsi, Ukraine).

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