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Ellipsometric detection of GaAs(001) surface hydrogenation in H_2 atmosphere

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ABSTRACT

Optical properties of MBE-grown GaAs(001) surfaces have been studied by spectroscopic ellipsometry under dynamic conditions of ramp heating and cooling after desorption of passivating As-cap-layer with low pressure H_2 atmosphere (14 Torr) applied to the surface. The temperature dependence of GaAs pseudo-dielectric function with atomically smooth (001) surface carrying the *fixed* Ga-rich (4×2) reconstruction was obtained for the temperature range of 160–600 °C. It is shown ellipsometrically that GaAs(001) heating in the molecular hydrogen atmosphere results in the formation of hydrogenated layer on the surface.

1. Introduction

Hydrogen plays a key role in a number of technological processes such as epitaxial crystal growth, defect passivation, surface cleaning and etching. Consequently, the interaction of hydrogen with $A^{III}B^{V}$ semiconductor surfaces has been studied intensively over the last 30 years [1]. It should be mentioned, however, that majority of experimental and theoretical results is connected with properties of atomic hydrogen (as more active). The number of papers devoted to molecular hydrogen is much less. At the same time with the evolution of MOCVD and CBE the information about the character of interaction between molecular hydrogen and growth surface becomes much more important, because the atmosphere of H_2 is the working one for these technologies albeit within greatly different pressure ranges.

As to GaAs(001) the issue still remains open whether H_2 interacts with surface under pressure of 10–760 Torr. About 10 years ago Li et al. [2] showed that using a high pressure of molecular hydrogen typical for MOCVD during the annealing changes dramatically the sequence of reconstruction states of the GaAs(001) surface: $(1 \times 2)/c(4 \times 4) \Rightarrow (2 \times 4) \Rightarrow (4 \times 2)$. In addition, during the $(2 \times 4) \Rightarrow (4 \times 2)$ transition the coexistence of domains with As-rich (2×4) and Ga-rich (4×2) reconstructions is observed on the same surface, while (3×1) and $(n \times 6)$ reconstructions are missed. It should be noticed, that due to high hydrogen pressure the LEED and STM investigations of the surface reconstructions were carried out *ex situ*, after cooling and reloading the sample from MOCVD reactor to analytical camera. Therefore, it was possible that such manipulations could influence the sequence of surface superstructures. At the same time, Kamiya et al. [3] showed the identity of optical properties (RDS-spectra) of (4×4), (2×4), and (4×2) reconstructions, obtained during annealing in ultra-high vacuum (UHV) and in the H_2 atmosphere. And this is almost universally taken as unambiguous indication of the molecular hydrogen inertness to GaAs surface.

We have shown previously [4–6], that the appearance of (3×1), (1×6), (1×1), and (4×6) transitional reconstructions on the surface is accompanied by peculiar optical response, that can be fixed quite clearly by means of simple single-wavelength ellipsometry. Obviously, the spectroscopic ellipsometry is a much more informative tool in elucidating the surface processes occurring at the best available (in terms of chemical purity and morphological smoothness) GaAs(001) face which can be prepared by MBE.

Thus, the goal of this paper is the investigation of optical characteristics of atomically clean and smooth GaAs(001) surface during the heating in H_2 atmosphere by spectroscopic ellipsometry in situ.

2. Experimental

The investigations were carried out in the growth chamber of EMCORE MOCVD machine equipped by *in situ* spectroscopic ellipsometer M-44 J.A. Woollam Co. Ellipsometric measurement during the experiments were realized in the 424–746.4 nm wave-length range. Ellipsometric parameters ψ and Δ were measured with an accuracy of 0.01° and 0.1°, respectively. The angle of incidence of light beam on the sample surface was fixed at 70.29 ± 0.05°. The MOCVD reactor was filled up by molecular hydrogen of Pd-purity. The hydrogen pressure $P(H_2)$ during the investigations was about 14 Torr.

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The samples used were homoepitaxial layers of GaAs (~70 nm thick) grown by molecular-beam epitaxy on semi-insulating substrates oriented (001) within ±0.5° and capped by amorphous As layer (~40 nm thick) immediately after growth using As_2 beam from cracker-cell. After air transfer to MOCVD-chamber the clean surface was obtained by removing the As-cap-layer by heating the sample in H_2 atmosphere.

The heating of GaAs/a-As structures was realized radiationally and was controlled by chromel–alumel thermocouple, which was set into heating element (direct thermal contact with a sample was absent). The temperature variation during experiments consists of heating at a rate of 6 °C/min (from 250 to 700 °C), annealing at fixed temperature and cooling at a rate of 28 °C/min (from 700 to 20 °C).

3. Results and discussion

Experimental results can be divided into two basic regimes. During the first one the data are measured in the heating mode. These data characterize the processes concerning with the reconstructing changes on the surface and with the formation of hydrogen bonding. Among the second regime the data are measured during the cooling. They contain the information about temperature changes of bulk GaAs optical properties. Since the temperature dependence of optical transitions energies in Brillouin zone has been measured precisely for the majority of technologically important semiconductors, including GaAs [7,8], then the problem of surface temperature determination reduces to the calculation of critical points (CP) parameters from SE-measured spectra [9]. Results of this temperature determination procedure are shown in Fig. 1. The information acquired in this way was used for the calibration of thermocouple data. It allowed to obtain the temperature (160–600 °C) dependence of dielectric function for atomically smooth surface GaAs(001) with a *fixed* (4 × 2) reconstruction shown in Fig. 2.

In Fig. 3 the evolutions of ellipsometric parameters (at the same wavelength) are compared during ramp heating of decapped GaAs(001) in a vacuum chamber under low-intensity As_4 beam (Fig. 3a) and under molecular hydrogen atmosphere (Fig. 3b). The data of Fig. 3a were taken from our earlier publications [5,6] where special temperature calibration procedure was implemented for exact assignment of temperature intervals for different surface reconstructions observed, including transitory ones. As can be seen from Fig. 3 the behavior of GaAs(001) surface is strikingly different under vacuum (or As_4 beam) and in H_2 environment. No transitional reconstructions are observed for the case of hydrogen atmosphere. This result is in good agreement with Li et al. [2].

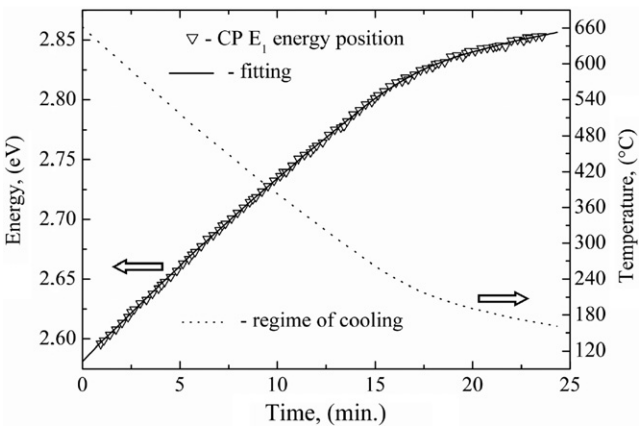

Fig. 1. The result of surface temperature determination procedure.

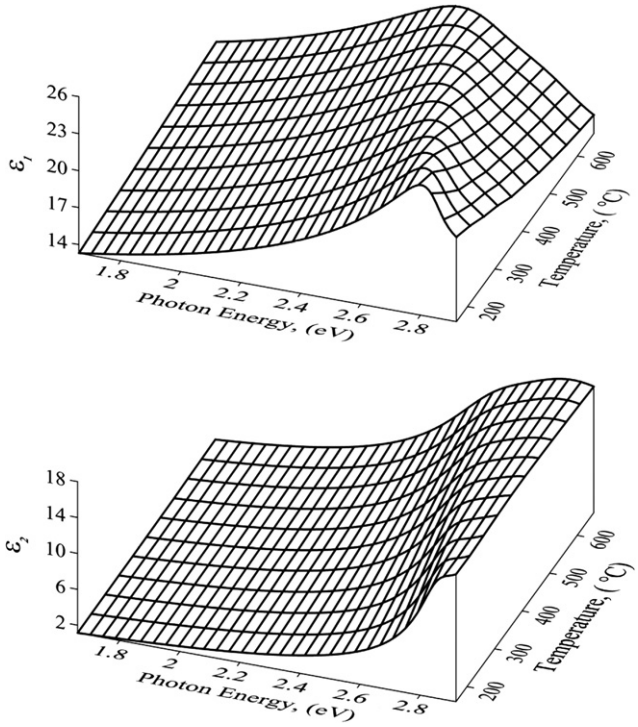

Fig. 2. The temperature dependence of pseudo-dielectric function for atomically smooth surface GaAs(001) with a fixed (4 × 2) reconstruction.

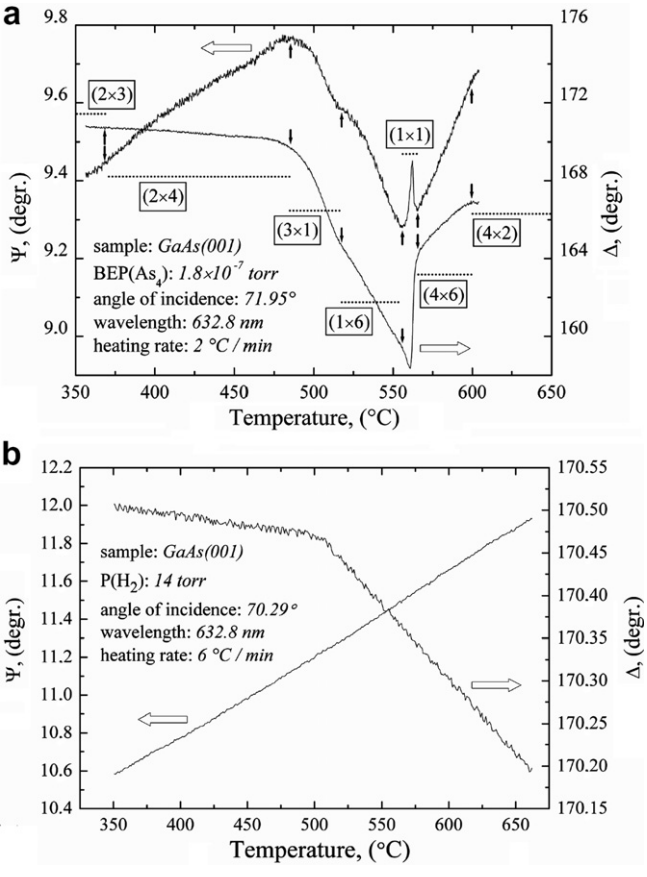

Fig. 3. The evolutions of ellipsometric parameters ψ and Δ during the heating of GaAs(001) surface in (a) As_4 vapor [5,6] and (b) H_2 atmosphere.