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Modification of the GaAs native oxide surface layer into the layer of the Ga_2O_3 dielectric by an Ar^+ ion beam

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ABSTRACT

Poor dielectric properties of GaAs oxides are the drawback of the GaAs-based electronics preventing using these oxides as dielectric layers. The elemental and chemical compositions of the GaAs native oxide layer slightly irradiated by Ar^+ ions with the fluence Q $\sim 1 * 10^{14}$ ions/cm^2 have been studied by the synchrotron-based photoelectron spectroscopy. The effect of selective and total decay of arsenic oxides followed by diffusive escape of arsenic atoms from the oxide layer has been revealed. The effect results in three-fold Ga enrichment of the upper layer of the native oxide and in strong domination (~90 at%) of the Ga_2O_3 phase which is known to be a quite good dielectric with the bandgap width as wide as 4.8 eV. A band diagram was obtained for the native oxide nanolayer on the *n*-GaAs wafer. It has been shown that this natural nanostructure has a character of a *p-n* heterojunction.

1. Introduction

GaAs-based semiconductors are ones of the most spread among A3B5 materials which have played an important role in modern high-frequency electronics due to their high electron mobility [1]. Therefore, research of GaAs oxides has remained topical for decades. Native, thermal and chemical oxides have been studied by a number of methods among which the surface sensitive X-ray photoelectron spectroscopy (XPS) was one of the most effective because of the small typical thickness (~2 nm) of the oxide layers [2–9]. It has been revealed that oxide layers arising or formed on the GaAs surfaces at relatively low temperatures ($T < 350\,^{\circ}C$) contain a mixture of dominant oxides such as Ga_2O_3, As_2O_3 and As_2O_5 [2,4,7]. The multiphase structure and relatively small bandgap width of the arsenic oxides make the GaAs oxides poor insulators with a high leakage current [1]. The GaAs oxides cannot play the same role of a technologically compatible dielectric in device structures as silicon oxide plays in the silicon electronics. Therefore, the problem of improving the dielectric properties of the GaAs oxides remains topical. One of the ways to solve the problem is thermal oxidation of the GaAs surface at the temperatures of 350–600 °C. High volatility of the As_2O_3 and As_2O_5 molecules results in enrichment of the thermal oxide layer in the Ga_2O_3 phase [2,4,8] which is known to be a sufficiently good dielectric with the bandgap as wide as 4.8 eV [10]. Enrichment of the thermal oxide layer in gallium by a factor of [Ga]/[As] ~1.45 has been observed [8], and the Ga-enrichment can be even greater at higher temperatures. Unfortunately, the use of this way is restricted by the decay of GaAs accompanied by evaporation of arsenic as well as by efficient diffusive smearing of the interfaces in device structures. Therefore, GaAs oxides formed at low temperatures, such as a native oxide naturally grown in air at room temperature, may prove to be promising as a dielectric for the GaAs-based electronics if the way of its enrichment in gallium is found. In this work, we investigated the native oxide nanolayer on the surface of the *n*-GaAs(100) wafer by XPS based on the synchrotron radiation. Almost three-fold growth of the Ga enrichment has been revealed in the upper layer of the native oxide. The observed enrichment occurs due to selective and total decay of the arsenic oxides in the GaAs native oxide layer under a low dose of an Ar^+ ion irradiation and results in strong domination of the Ga_2O_3 phase which is known to be a quite good dielectric. A band diagram was drawn for the native oxide nanolayer on the *n*-GaAs wafer which was shown to have a character of a *p-n* heterojunction.

2. Materials and methods

The experiment was performed in ultrahigh vacuum at the Russian–German synchrotron radiation beamline of the BESSY-II electron storage ring (Berlin) [11] by using a photoelectron spectrometer

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("Mustang") equipped with the hemispherical analyzer SPECS Phoibos 150 (SPECS GmbH). The photoelectron (photoemission) spectra were measured normally to the sample irradiated by a monochromatic *X*-ray photon beam at the angle $\theta = 55^o$. The spectra were measured at photon energies $h\nu = 150$ eV and $h\nu = 650$ eV. The photon energy scale of the plane-grating monochromator (RG-PGM) was regularly calibrated using the Au $4f_{7/2}$ line of gold in order to maintain the accuracy of the binding energy determination better than ± 0.05 eV. The analyzer operating mode was chosen for the major part of measurements so as to provide high sensitivity and statistics, though with sufficiently high energy resolution of $\Delta E < 300$ meV. The better resolution $\Delta E \sim 150$ meV was also used in determining the valence band edge position.

A commercial GaAs (100) *n*-type ($n \sim 10^{18}$ cm^{-3}) VGF wafer was used. A sample was etched in the high vacuum chamber of the LHS-11 (Leybold AG) spectrometer [12] before the BESSY-II experiment by Ar^+ ions with energy $E_i = 2500$ eV and fluence $Q \sim 5 * 10^{15}$ ions/cm^2 in order to remove the native oxide layer and form an atomically clean reference surface. This procedure is known to unify the surface layer of GaAs, resulting in formation of reproducible properties of the layer characterized by an essentially amorphized structure and some enrichment in gallium atoms [13–15]. The energy of Ar^+ ions ($E_i = 2500$ eV) was taken high enough to prevent large surface enrichment in gallium. Then the sample was naturally oxidized again and kept in dry atmosphere for several months to form a reproducible native oxide layer. Just before the measurements, the sample was kept for several hours in the high vacuum chamber of the "Mustang" spectrometer to reduce the thickness of water- and carbon-containing adsorbate. The native oxide layer was slightly irradiated by Ar^+ ions with energy $E_i = 2500$ eV and fluence $Q \sim 1 * 10^{14}$ ions/cm^2. The latter value was chosen so that an essential part of chemical bonds was broken without sputtering and visible changes in elemental composition of the oxide layer. The projected range of the irradiating ions ($R_p = 3.6$ nm) calculated using the commonly known SRIM 2006 code [16] exceeded the thickness of the native oxide layer (∼2 nm). After studying the oxide layer, the sample was etched again by the same Ar^+ ion beam to obtain the atomically clean GaAs reference surface for controlling the known binding energies and the procedure of elemental composition determination.

3. Results and discussion

Elemental composition and purity of the sample can be estimated from the photoelectron spectra measured in a wide electron binding energy range. Fig. 1 represents the survey spectra of the slightly irradiated native oxide layer (GaAs-oxide, solid line) and of the GaAs reference surface after etching the spectrum (GaAs, dotted line) by Ar^+ ions. (The initial unirradiated spectrum, which is not shown here, coincides with the slightly irradiated one, excepting the C1s carbon line.) The binding energy scale of the spectra is referred to the Fermi level. The spectra contain only the expected lines of gallium, arsenic and oxygen in the near surface layer. Some traces of the implanted argon ions are also seen. The C1s line of the carbon containing adsorbate is virtually absent in the spectrum of the native oxide since the fluence of the irradiating Ar^+ ions was sufficient to remove the adsorbate remained after keeping the sample in vacuum. The reference spectrum exhibits virtual absence of the O1s line, which evidences removal of the native oxide layer. The information (probing) depth in the GaAs sample analysis is determined by the escape depth of the Ga3d and As3d photoelectrons corresponding to the most intense lines of the spectra. The depth is of the order of the photoelectron mean free path which is equal to $\lambda \sim 2.5$ nm for photons with energy $h\nu = 650$ eV [17]. This depth slightly exceeds the native oxide layer thickness. Comparison of the Ga3d and As3d line intensities for the GaAs oxide and GaAs reference surfaces shows an insignificant rise in the average Ga concentration ([Ga]/[As] → 1.25) in the entire oxide layer with some contribution of the GaAs substrate. This observation implies insignificant changes in the gallium to arsenic ratio due to oxidation of the GaAs wafer followed by slight ion irradiation. To exclude the substrate contribution and check the elemental depth homogeneity of the oxide layer, the Ga3d and As3d photoemission spectra were measured at a lower photon energy ($h\nu = 150$ eV). The mean free path $\lambda \sim 1.0$ nm of these photoelectrons is essentially shorter thus restricting the information depth to the 1.0 nm near-surface layer of the GaAs-oxide.

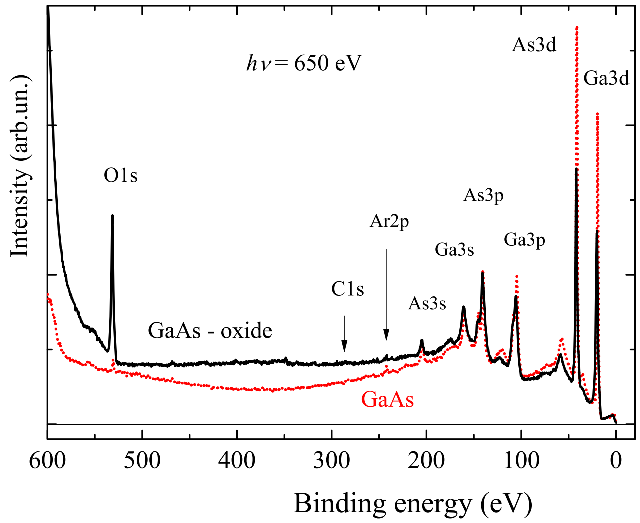

Fig. 1. Survey photoelectron spectra of a pristine *n*-GaAs (100) wafer covered by a layer of native oxide (GaAs-oxide, solid line) slightly irradiated by Ar^+ ions with fluence $Q \sim 1 * 10^{14}$ ions/cm^2 and of the same sample after removal of the oxide layer by the Ar^+ ion beam with fluence $Q \sim 5 * 10^{15}$ ions/cm^2 (GaAs, dotted line). Ar^+ ion energy $E_i = 2500$ eV. Photon energy $h\nu = 650$ eV.

Fig. 2 shows Ga3d photoelectron spectra measured in a narrow binding energy range before (Ga_2O_3) and after (GaAs) ion etching. The spectra clearly reveal the oxidation chemical shift. The Ga3d line of the ion-etched reference GaAs surface consists of an unresolved doublet ($3d_{3/2,1/2}$). The averaged binding energy E_B(Ga3d) = 19.3 eV of this line almost fully coincides with our former data [18,19] and proves to be consistent with literature data [20]. The spectrum of the oxidized surface consists of a broad peak centered at the energy $E_B = 20.5$ eV corresponding to oxide Ga_2O_3 [20]. This observation confirms the

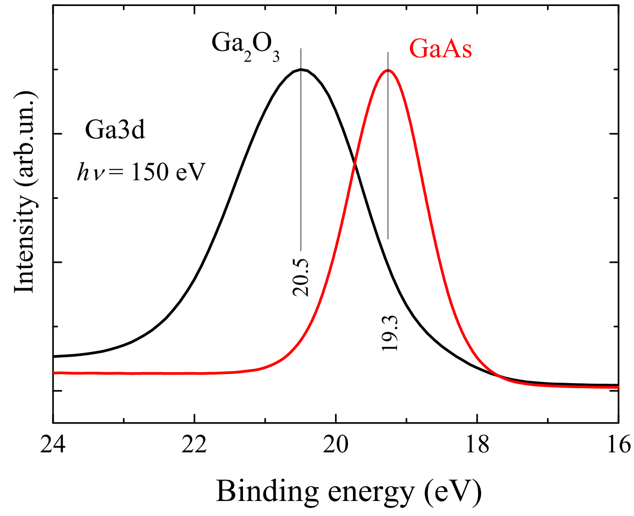

Fig. 2. Ga3d photoemission spectra of the *n*-GaAs (100) wafer with a layer of native oxide (20.5 eV) slightly irradiated by Ar^+ ions with energy $E_i = 2500$ eV and of the same sample after removal of the oxide layer by the Ar^+ ion beam (19.3 eV). The spectra were normalized to the maximum. Photon energy $h\nu = 150$ eV.