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Native oxides formation and surface wettability of epitaxial III–V materials: The case of InP and GaAs

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ABSTRACT

The time dependent transition from hydrophobic to hydrophilic states of the metalorganic vapour phase epitaxy (MOVPE) grown InP, GaAs and InAs is systematically documented by contact angle measurements. Natural oxides forming on the surfaces of air-exposed materials, as well as the results of some typical wet chemical process to remove those oxides, were studied by X-ray photoemission spectroscopy (XPS), revealing, surprisingly, a fundamental lack of strong correlations between the surface oxide composition and the reported systematic changes in hydrophobicity.

1. Introduction

Binary alloys like InP, GaAs and InAs are the most elementary and common III–V semiconductors grown by metalorganic vapour phase epitaxy (MOVPE) and other techniques, being widely used in many devices, and can represent "basic" structures from which properties of other III–V materials and alloys can be deduced. Their physical-chemical properties play a very important role, as they determine device performances, even when they are being used as cladding layers, i.e. interfacing the device to the environment, or when subsequent overgrowth is planned, or simply when surface sensitive processing is performed. Specifically, air exposure of epitaxial binaries (and compounds) causes gradual formation of native oxides on the material surface, which can be composed of various crystalline and amorphous forms of e.g., $InPO_4$, $InPO_3$, In_2O_3 for InP; Ga_2O_3, As_2O_3, and $GaAsO_4$ for GaAs and In_2O_3, As_2O_3 in case of InAs, as broadly reported in the scientific literature [1–5]. This can lead to problems at various levels. For example, a long storage time for both GaAs [6] and InP [7] epi-ready wafers can have negative impact on the quality of the overgrowth, with possible issues in removing the oxides from the substrate surface with standard deoxidation processes. Or, ageing can affect the surface chemical properties [8], possibly changing device processing "paths" with detrimental device reproducibility.

In this context, we have shown that long term oxidation processes affect the nature of water/solid interface of GaAs surfaces [9], reflecting a non-trivial (and fundamentally unreported) change of surface chemistry. In this paper we present a broader and more comprehensive comparative study of the effects on the water/solid interface of air exposed relevant binary compounds (InP, GaAs and InAs), followed by an investigation by means of X-ray photoelectron spectroscopy (XPS) seeking possible correlations with the oxide formation on all these materials.

We importantly show that a number of interpretations presented in the literature linking surface wettability and surface oxide composition are at least incomplete, and further experimental and theoretical re-evaluation on these topics is desirable, as well as broader consideration of factors contributing to the liquid-solid interface, other than simply just the oxidation state.

2. Experimental details

All samples were epitaxially overgrown by MOVPE. Their surfaces showed morphologies with typical step ordering for MOVPE (step flow and/or step bunching), which, as recently clarified, is caused by the two-step process of decomposition and diffusion of precursor species and the subsequent adatom diffusion and incorporation [10,11]. All growth runs for the samples described in this work were carried out at low pressure (80 mbar) in a

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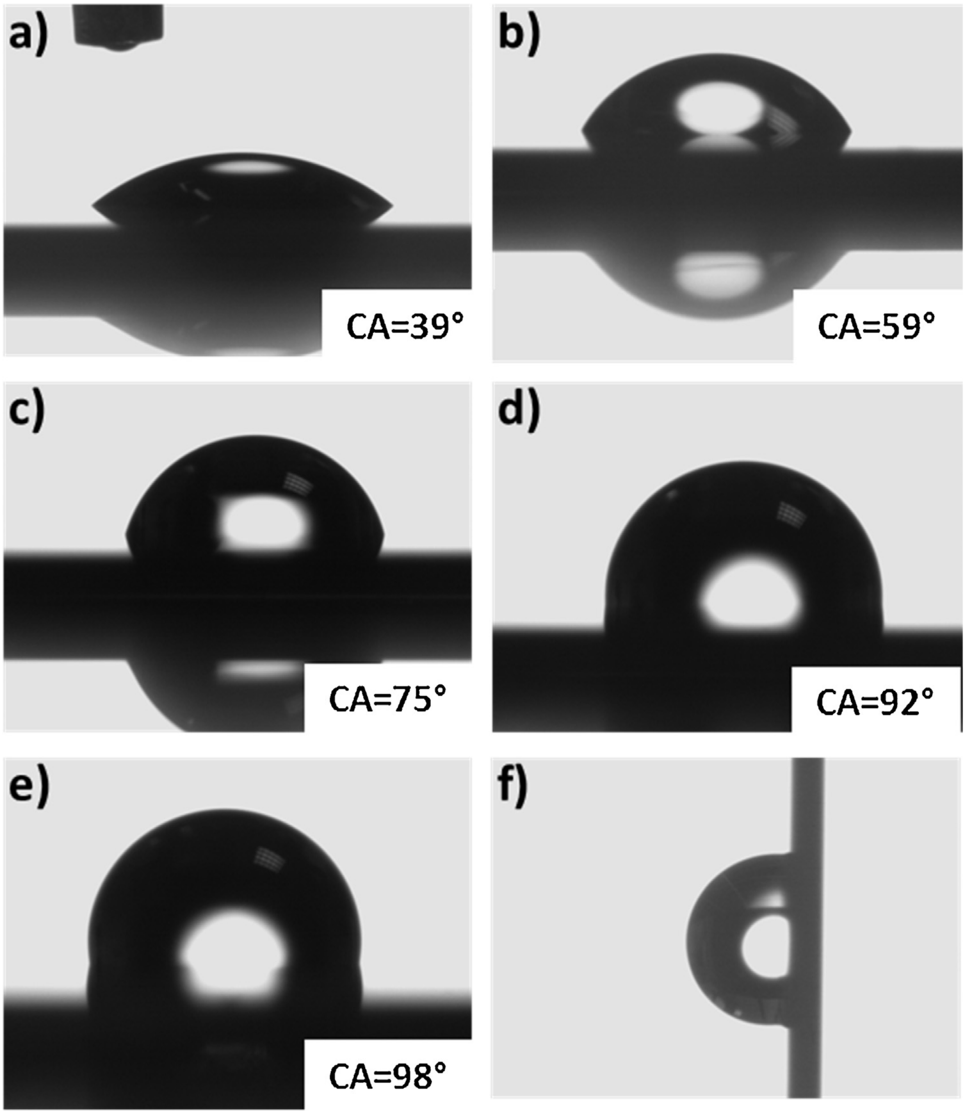

Fig. 1. Representative water drop contact angle on air exposed epitaxial InP; a) fresh, contact angle (CA) = 39°; b) 1 day old, CA = 59°; c) 6 days old, CA = 75°; d) 1 month old, CA = 92°; e) and f) 6 months old, in two different geometries, CA = 98°, and "petal effect" evidence, the droplet does not slide away. There is a clear trend towards higher contact angles with ageing, with hydrophobicity threshold crossed after 1 month of storage.

commercial horizontal reactor with purified N_2 as carrier gas [12]. The structures were grown on (001) GaAs, (001) InP or (100) InAs perfectly oriented or slightly misoriented substrates [13]. The precursors were trimethylgallium (TMGa), trimethylindium (TMI), arsine (AsH_3) and phosphine (PH_3). Growth conditions were selected for "best" practice/quality material, following our previous studies and our lab state-of-the-art [14–16].

All epitaxial growths resulted in smooth, mirror-like surfaces, which were subsequently investigated with Atomic Force Microscopy (AFM) in tapping mode for quality control. Water drop contact angle (WDCA, or CA for short) measurements were conducted to determine hydrophilic/hydrophobic properties of the surface. 1 μl of deionised water (DI) was dispensed by microsyringe on the sample surface and the contact angle of the formed sessile drop was measured. The profile of the droplet was recorded by a computer-controlled system and the contact angle was taken as the angle between the substrate surface and tangent to the droplet surface at the substrate/droplet/air interface. Multiple measurements were taken from a single sample, showing less than 2° deviation from the average value. The terms "hydrophobic", "hydrophilic" and "superhydrophilic" are used to describe materials showing WDCA of >90°, <90° and <5°, respectively. This is important to note, as in many literature reports [17] those terms are used quite liberally, referring to different WDCA values or sometimes to simple observations without actually determining the contact angle at all, as well as referring to the easiness of flushing the material surface with a liquid, confusing contact and sliding angles (which is defined as the critical angle at which a water droplet of a given weight begins to slide down the inclined surface).

Measurements were conducted on "fresh" material (within 30 min after removal from the MOVPE reactor), and then repeated after 1 day, 7 days, 30 days and several months of storage in an ambient atmosphere. It is worth noticing here that the results are fully reproducible and independent of the storage carrier we used and tested (e.g. Fluoroware, polystyrene, glass), and that unintentional surface contamination (other than that induced by "normal" air exposure, however and admittedly not "rigorously" defined) should not be considered as the source of what we report. The oxygen plasma treatment was conducted in a Diener Electronic FEMTO Plasma System, at 50 W and at 0.2 mbar for the time specified in the text. Wet chemical etching was performed by dipping the samples into 37% HCl or 48% HF aqueous solutions and then rinsing with DI