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Reflectance and reflectance anisotropy measurements of the photoelectrochemical deposition of gold on p-type gallium arsenide (100) electrodes

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Abstract. The photoelectrochemical deposition of gold on p-type GaAs has been monitored *in situ* via the total reflectance response and reflectance anisotropy of the nascent surface. It is demonstrated that the former method probes the macroscopic deposition rate while the latter method probes surface ordering in the growing layer. For the system studied here, the RA data are most consistent with a highly anisotropic initial gold layer, such as may be expected from a single-crystalline film. This proposal is shown to be in good agreement with electron diffraction data for the GaAs/Au interface, which indicate that the initial gold deposit adopts a (110) orientation in which the lattice parameter of the gold film matches that of the GaAs (100) substrate.

1. Introduction

The introduction of laser-based diagnostic techniques to the study of materials growth by chemical vapour deposition and related methods has gained importance in recent years. In particular, several groups have employed both reflectance methods [1] and also the more sophisticated method of reflectance anisotropy (RA) [2–6] in order to probe the growth of III–V layers by molecular beam epitaxy and metallorganic vapour phase epitaxy. These studies have, to date, been carried out under relatively low-pressure conditions. We believe that as optical techniques, they are generally applicable to the study of deposition processes and should not be restricted to studies of the interface between the gas phase and a growing surface.

In this brief communication, we report reflectance measurements carried out during the photoelectrochemical deposition of metallic gold on p-type GaAs electrodes in an aqueous solution. In particular, we report what are believed to be the first reflectance anisotropy measurements recorded *in situ*, from a semiconductor electrochemical system, which demonstrate the viability of reflectance methods for the real-time study of processes occurring at semiconductor electrodes and can provide information on both the extent of surface deposition and structural information on the adlayer.

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2. Experimental procedure

Electrochemical deposition was carried out in a conventional three-electrode cell in which the p-GaAs (100) sample, (orientation 2 degrees towards ⟨110⟩), formed the working electrode, the counter electrode was formed by Pt foil and the reference electrode was saturated calomel. The electrolyte was an aqueous solution of 0.001 molar $K[AuCl_4]$ supported in 0.1 molar KCN. A potentiostat (Kemitron 543) was used to control the working electrode and also to monitor the cell current. Total reflectance measurements were carried out by modulating either the output of a Krypton ion laser (Coherent Innova 90) or Argon ion laser (Spectra Physics 165) with a rotating disc optical chopper (Scitech) and allowing the modulated beam to impinge on the electrode at near normal incidence. The reflected light was detected by a photodiode and the resultant signal processed via either a lock-in amplifier/microcomputer (Stanford Research Systems/Amstrad PCW) or a lock-in amplifier/chart recorder combination. The lasers were operated on the 647 and 351 nm lines respectively. Reflectance anisotropy measurements were carried out by the introduction of a polarization modulator, namely a Pockels cell, into the experimental geometry. The Pockels cell (Electro-optics Development) was driven by a modulator (in-house construction) and the resultant modulation decoded using a lock-in amplifier (also in-house construction) the output of which was fed into the commercial lock-in (figure 1).

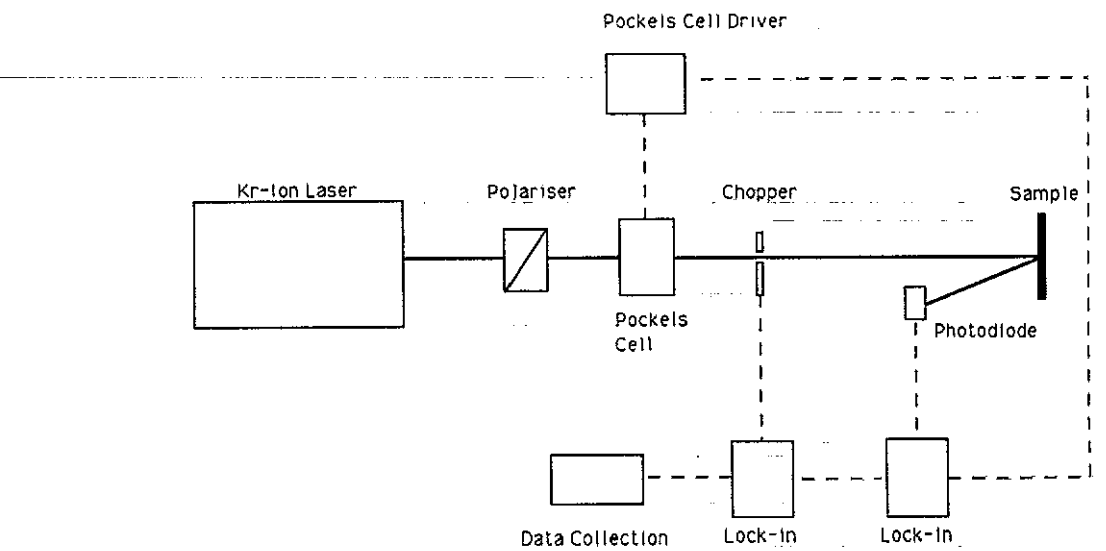

Figure 1. Schematic diagram of the apparatus used for the reflectance and reflectance anisotropy measurements.

3. Results and discussion

Figures 2(*a*) and (*b*) depict the total reflectance and reflectance anisotropy respectively from of a p-type GaAs electrode in the aqueous gold III solution at potential of −1 V SCE, as a function of deposition time, for irradiation at 647 nm.

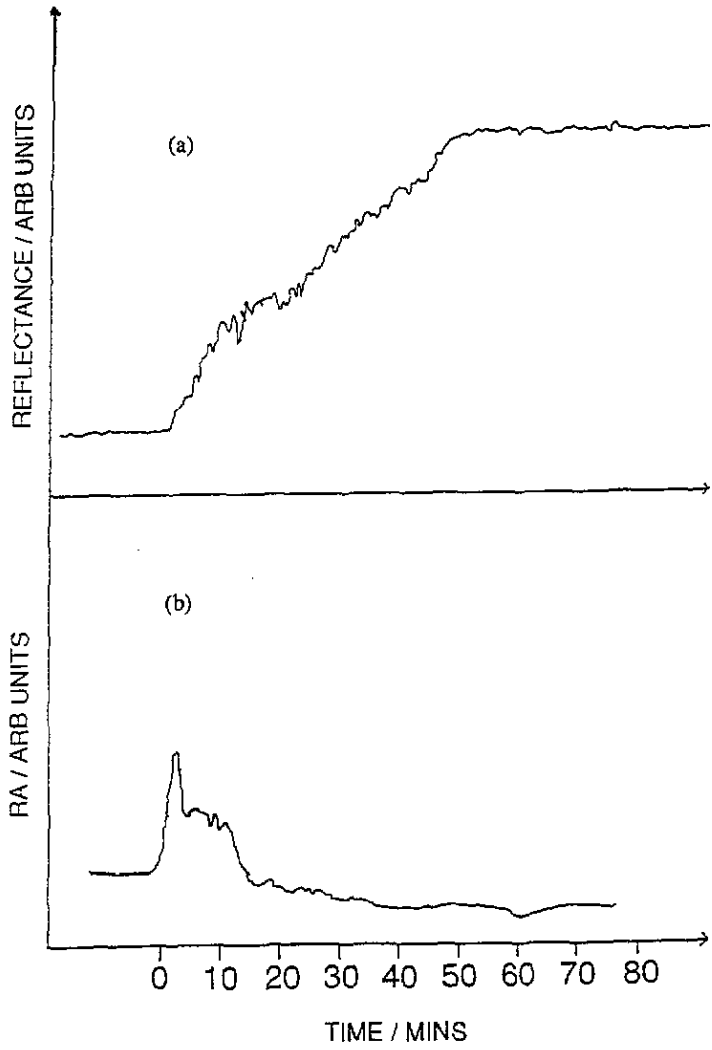

Figure 2. (*a*) Reflectance, and (*b*) reflectance anisotropy at 647 nm, recorded from the surface of a p-type GaAs (100) electrode in aqueous gold III solution at a potential of −1 V SCE, as a function of time. The laser operating power was approximately 60 mW, unfocussed.

Figures 3(*a*) and (*b*) are the analogous data for irradiation at 351 nm. Figure 2(*a*) shows a steady increase in surface reflectivity starting almost simultaneously with the application of a cell potential, the value growing steadily and reaching a final value some 50 minutes after the start of deposition. Figure 3(*a*) shows a steady decrease in surface reflectivity commencing simultaneously with the application of a cell potential which appears to stabilize at around 25 minutes. Reflectance anisotropy data for the deposition of gold are presented in figures 2(*b*) (647 nm) and 3(*b*) (351 nm). Examination of these plots reveals that in both cases the most dramatic changes occured in the time period immediately after the application of the cell potential. For the case of 647 nm irradiation an initial increase in the RA signal was followed by a dramatic fall and the gradient leveled off, increases and drops at around 15 minutes,

remaining fairly constant over the rest of the deposition period. The sign of the changes could be reversed by adjusting the orientation of the electrode such that the crystal axes were rotated by 90°. In the case of the ultra-violet excitation (figure 3(*b*)) an initial increase in RA signal was followed by a dramatic decrease which bottomed out at around 8.5 minutes and was followed by a slight rise with some oscillatory behaviour for the remaining deposition period.

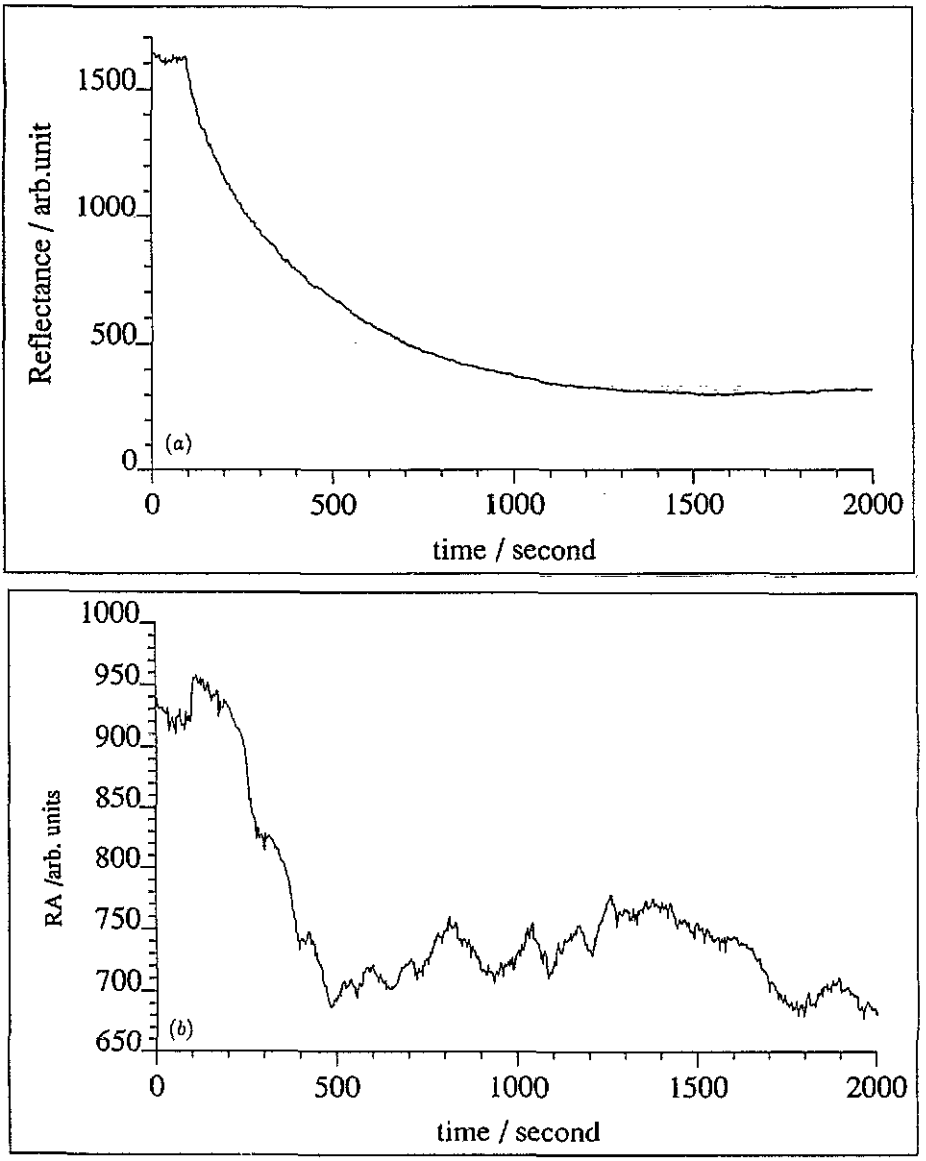

Figure 3. (*a*) Reflectance, and (*b*) reflectance anisotropy at 351 nm, recorded from the surface of a p-type GaAs (100) electrode in aqueous gold III solution at a potential of −1 V SCE, as a function of time. The laser operating power was approximately 5 mW, unfocussed.

The total reflectance data can be interpreted in terms of the bulk behaviour of

GaAs and gold. In both cases the radiation is significantly above the band gap of the semiconductor and it is the absorption of radiation that gives rise to the photogenerated surface electrons used in the electrochemical deposition. Deposition of gold which is highly reflective at 647 nm gives rise to a steady increase in the intensity of the reflected light as the electrode behaves initially like GaAs, then intermediately, and finally like gold metal. Similarly under UV irradiation the initial absorption of radiation by GaAs is gradually enhanced by the deposition of gold. The gold plasmon resonance is known to absorb here [7] and the gradual deposition gives rise to the increase in extinction coefficient for the film/electrode combination and a subsequent loss of intensity of reflected light. This behaviour has the implications that as deposition proceeds the sensitivity of the RA technique increases for red illumination and decreases for UV illumination, since the signal to noise ratio is highly dependent upon the reflected photon flux.

The RA data show changes that occur on a timescale different to the total reflectance measurements and that 'saturate' relatively early in the deposition process. Previous studies [8] have shown by electron microscopy that this deposition is characterized by two specific domains. Initially a highly ordered polycrystalline form of gold is deposited such that growth occurs along a (110) direction in order to accommodate the lattice mismatch between gold and GaAs. In the later stages, amorphous gold is deposited and finally saturates when the excitation can no longer promote the surface electrons for this process. The initial crystalline growth is highly ordered and would be expected to show a reflectance anisotropy.

4. Conclusions

We have demonstrated for the first time that reflectance anisotropy may be used as a simple *in situ* probe for monitoring in real time the ordering of surface layers during electrochemical deposition. Additionally in this work we have shown that simple reflectance measurements are potentially capable of monitoring total deposition rate.

Acknowledgments

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