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A STUDY OF ANODIC FILMS ON N-TYPE INP BY SPECTROSCOPIC ELLIPSOMETRY AND ATOMIC FORCE MICROSCOPY

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ABSTRACT

The growth of anodic films on n-InP in 1 mol dm^{-1} KOH is investigated under potential sweep conditions. At lower potentials a thin surface film is formed and a peak is observed on the current-voltage curve. Ellipsometric measurements show that this film increases in thickness with increasing potential but the observed thickness values are significantly less than the corresponding coulometrically estimated values. This indicates that much of the charge passed is not involved in the formation of a surface film but presumably in the formation of soluble anodic reaction products. Cyclic voltammograms show that a current peak is also observed on the reverse sweep and ellipsometric measurements show that the anodic film thickness also increases during the reverse sweep until the peak potential is reached. Atomic force microscopy (AFM) shows that the surface becomes smoother as the potential is increased. We attribute this to the formation of nuclei at lower potentials, which coalesce as the layer becomes thicker. Electron diffraction and x-ray photoelectron spectroscopy (XPS) analysis show that the surface film is predominantly In_2O_3 with no evidence of $InPO_4$.

INTRODUCTION

III–V semiconductors such as GaAs and InP have been the subject of a large number of investigations and are used to fabricate a variety of devices used for optical communications and high-speed electronic systems.[1] In order to develop these technologies, the growth of coherent oxides on the surface of III–V compounds is often desirable in device fabrication. For example, such oxide films are useful as surface passivating layers in the fabrication of both optoelectronic devices and field effect transistors[2,3].

GaAs, in particular, has been extensively studied[1,4,5] by a variety of surface-analytical techniques[6-8] and the growth of anodic films on InP has also been extensively

investigated[9-18]. Although marked differences emerge in these studies concerning the detailed composition of the films, it is evident that films often consist of two distinct layers: an outer indium-rich layer, and an inner phosphorus-rich layer. In contrast to Si, however, the thermal oxide formed on InP is of low quality and tends to be too conductive for use as a gate insulator. In comparison with thermal oxidation, anodic oxidation results in a significant improvement in electrical properties. Anodic oxidation is useful since it is capable of providing uniform layers of oxide with a smooth interface at room temperature.

Although anodic oxide growth on InP has been studied extensively under a wide variety of conditions using surface analytical techniques[8,19], relatively little work has been conducted on the relationship between the current-voltage characteristics of the anodic process and the growth characteristics of the surface oxide. We recently reported on the observation of porous InP formation under anodic conditions in KOH electrolytes[20-22]. The characteristics of the porous layer were noted to be affected by the concentration of KOH[23]. Furthermore, we showed that anodization in 1 mol dm^{-3} results in anodic film formation rather than porous InP formation[22,24,25]. At lower potentials, a thin compact surface film is formed while at higher potentials a thick, porous anodic film is formed.[22,25] The results presented here concern a detailed investigation of thin anodic film formation at lower potentials in 1 mol dm^{-3} KOH.

EXPERIMENTAL

The working electrode consisted of polished (100)-oriented monocrystalline sulfur doped n-InP with a carrier concentration of $\sim 3 \times 10^{18}$ cm^{-3}. Alloying indium to the InP sample made an ohmic contact and the contact was isolated from the electrolyte by means of a suitable varnish. The electrode area was typically 0.2 cm^2. Anodization was carried out in aqueous KOH electrolytes with a concentration of 1 mol dm^{-3}. A conventional three-electrode configuration was used employing a platinum counter electrode and saturated calomel reference electrode (SCE) to which all potentials are referenced. Prior to immersion in the electrolyte, the working electrode was dipped in a 3:1:1 H_2SO_4:H_2O_2:H_2O etchant and rinsed in deionized water. All of the electrochemical experiments were carried out at room temperature and in dark conditions.

A CH Instruments Model 650A Electrochemical Workstation interfaced to a Personal Computer (PC) was employed for cell parameter control and for data acquisition. Slices for cross-sectional microscopic analysis were prepared by thinning to electron transparency using standard focused ion beam milling procedures by means of a FEI 200 FIBSIMS workstation. The transmission electron microscopy (TEM) characterization was performed using a JEOL 2010 TEM operating at 200 kV. All AFM data was acquired after anodization using a Topometrix Explorer. Spectroscopic ellipsometry was performed using a J.A. Woollam Co., Inc. M-2000 U spectroscopic ellipsometer. All data was acquired over a wavelength range of 250-800 nm.

RESULTS AND DISCUSSION

Thin Film Growth

Fig. 1 illustrates a linear sweep voltammogram of an InP electrode in 1 mol dm^{-3} KOH from 0.0 V to 2.0 V at a scan rate of 2.5 mV s^{-1}. Very little current flow is observed in the potential range 0.0 V to 0.6 V. As the potential is increased further, however, the current density begins to increase reaching a peak current density of 5 mA cm^{-2} at 1.04 V. Above 1.04 V, the current density decreases, reaching a value of 3.5 mA cm^{-2} at 1.25 V where a pronounced knee occurs on the curve. Thereafter, the current is observed to decrease more slowly reaching a value of 2.5 mA cm^{-2} at 2.0 V. Similar results were obtained at scan rates of 5 mV s^{-1} and 10 mV s^{-1}.

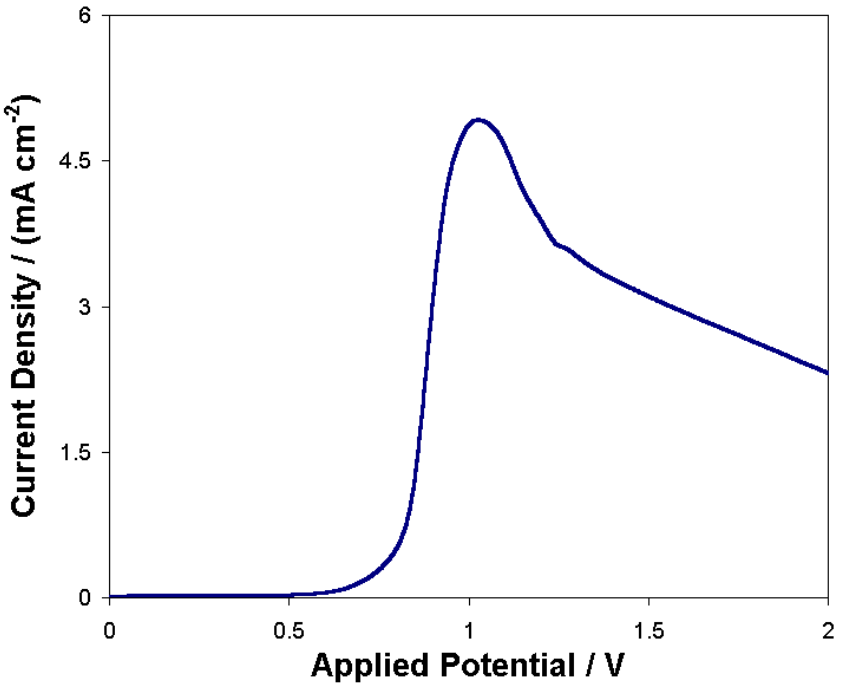

Fig. 1 *Linear sweep voltammogram of an n-InP electrode in 1 mol dm^{-3} KOH from 0.0 V to 2.5 V (SCE) at a scan rate of 2.5 mV s^{-1}.*

Visual inspection and examination by optical and scanning electron microscopy of the surface of an InP electrode after anodization in 1 mol dm^{-3} KOH from 0.0 V – 1.0 V gave no indication of any appreciable surface modification. Cross-sectional TEM was employed to characterize the surface film. Fig. 2 shows a cross-sectional TEM micrograph of the InP electrode after being subjected to a potential sweep in 1 mol dm^{-3} KOH from 0.0 V to 1.2 V at a scan rate of 10 mV s^{-1}. It is observed that a thin, compact film has formed on the surface of the electrode with an estimated thickness of ~25 nm.

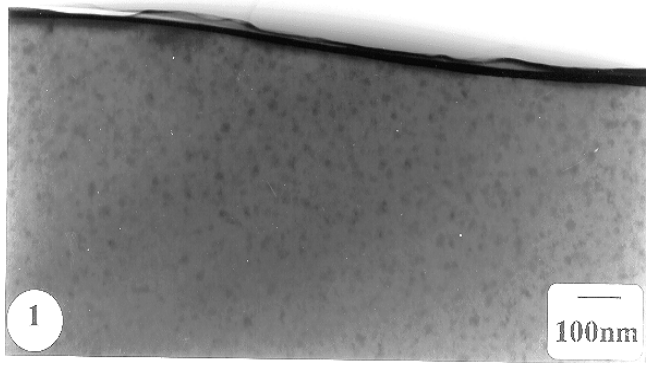

Fig. 2 *Bright field through focal cross-sectional TEM micrograph of an InP electrode after a potential sweep from 0.0 V to 1.2 V at a scan rate of 10 mV s^{-1} in 1 mol dm^{-3} KOH.*

Ellipsometric Measurements

Spectroscopic ellipsometry was employed to characterize this anodic film. After anodization, the electrode was rinsed and the ellipsometric data was acquired *ex-situ* with incident angles of 70^0, 75^0 and 80^0 in the wavelength range 350 – 850 nm. Film thickness was determined, assuming a single, compact In_2O_3 layer. Ellipsometric measurements were acquired at a variety of points on the surface to determine the uniformity of the film thickness. A thickness value of 26.5 nm was estimated from the ellipsometric data in agreement with the film thickness measured using TEM (~25 nm) as shown in Fig. 2.

For comparison, ellipsometric characterization was also conducted on (1) the as-received InP, (2) the etched InP surface prior to immersion in the electrolyte and (3) after dipping in the electrolyte for various lengths of time without the application of a bias. The as-received surface was found to be covered with a thin native oxide ~3.5 nm in thickness. After etching, this oxide thickness was reduced to ~1.2 nm indicating a reduction in the thickness of oxide present prior to anodization. Furthermore, ellipsometric characterization of the surface after etching and dipping in KOH for 5 s showed that no appreciable oxide formation occurs prior to anodization.

Thus, the results throughout this work pertain to oxide growth as a function of applied potential. A series of potential sweep experiments were carried out from 0.0 V to upper potential limits in the range of 0.6 V to 1.2 V at scan rates of 10 mV s^{-1}, 5 mV s^{-1} and 2.5 mV s^{-1} respectively. After anodization, ellipsometric data was acquired for each sample. Film thickness was determined as outlined above and the values obtained are plotted in Fig. 3 against the upper limit of the potential sweep. It is observed that film thickness increases with potential for a given scan rate and, for a given potential, the films grown are thicker if formed at slower scan rates. Maximum values of anodic film thickness were estimated coulometrically from values of the charge density, Q, obtained by integration of the current densities in voltammograms such as Fig. 1 with respect to

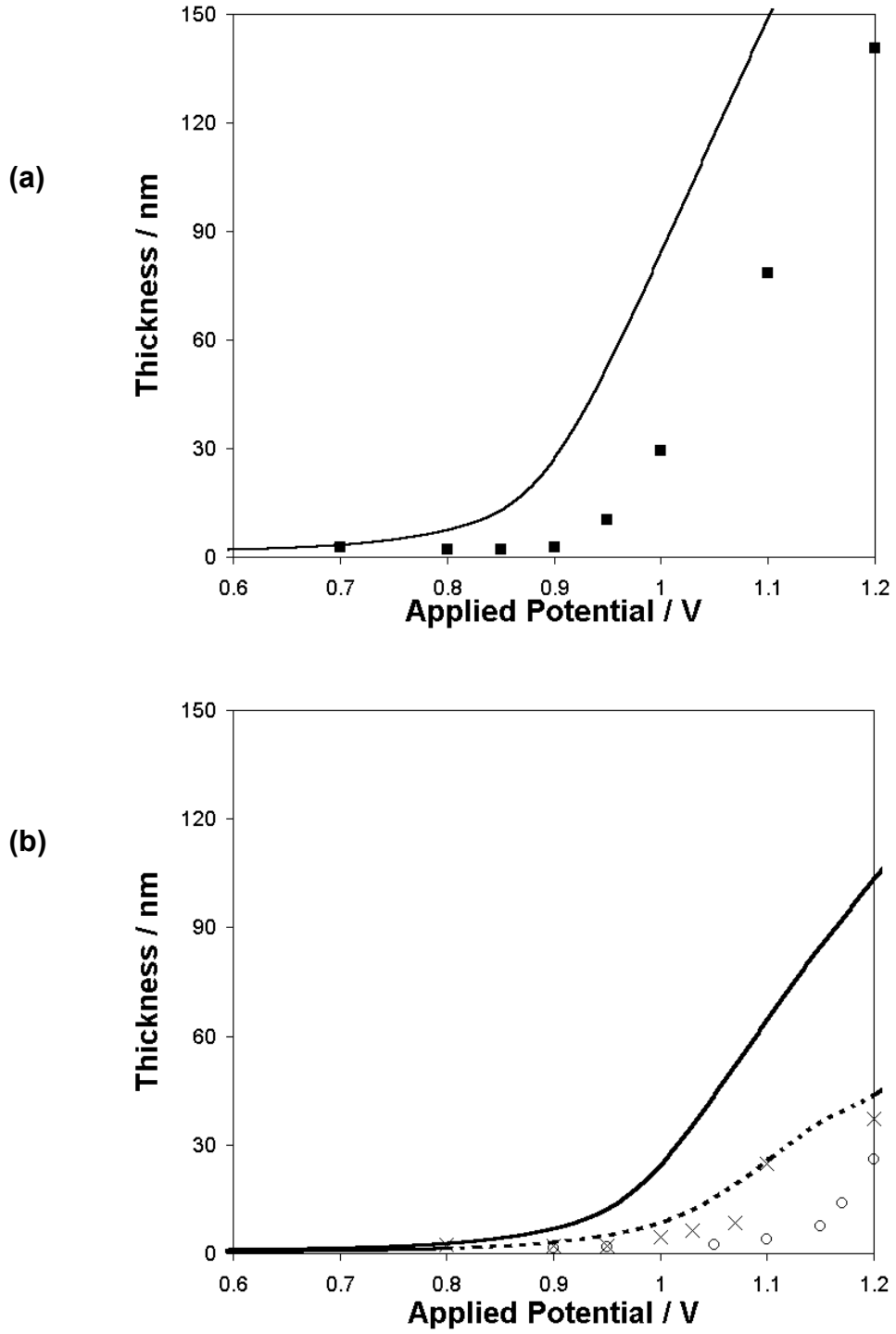

Fig. 3 *(a): Coulometrically estimated film thickness (—) based on the charge passed during the potential sweep in 1 mol dm^{-3} KOH at 2.5 mV s^{-1}. Values of ellipsometrically estimated film thickness at various potentials along sweep also shown (■). (b): Coulometrically estimated film thickness based on the charge passed during the potential sweep in 1 mol dm^{-3} KOH at 5 mV s^{-1}(—) and 10 mV s^{-1}(···). Ellipsometrically estimated thickness for 5 mV s^{-1}and 10 mV s^{-1}, (×) and (o) respectively. The lower limit of all potential sweeps was 0.0 V (SCE).*

time. We assume an electrochemical process such as

$$InP + 11OH^- \rightarrow \tfrac{1}{2}\, In_2O_3 + 11/2\, H_2O + PO_4^{3-} + 8e^- \qquad (1)$$

leading to the formation of an In_2O_3 film and dissolved oxo anions of phosphorous. The formation of PO_4^{3-} (a P^V oxo anion) as written in Eqn. 1 corresponds to an 8-electron (per InP) process while, for example, the formation of a P^{III} oxo anion such as HPO_3^{3-} corresponds to a 6-electron process. From Faraday's law, the thickness, *d*, obtained assuming that all of the current passed is involved in compact film formation is given by

$$d = \frac{V_{m(In_2O_3)}Q}{2nF} \qquad (2)$$

where *d* is the film thickness, $V_{M(In_2O_3)}$ is the molar volume of In_2O_3, *F* is the Faraday constant and *n* is the number of electrons transferred per formula unit of InP. Values of film thickness were estimated in this way using a value[26, 27] of $V_{M(In_2O_3)}$ = 38.66 cm^3 and assuming *n* = 8 and are plotted in Fig. 3 also.

Comparing the ellipsometrically estimated and coulometrically estimated thickness values in Fig 3(a) it is observed that, except at lower potentials, the ellipsometrically measured thicknesses are considerably less than the coulometrically estimated thicknesses. This indicates that much of the charge passed is not involved in the formation of a surface film but presumably in the formation of soluble anodic reaction products. Fig 3(b) shows that a similar pattern of results is obtained at higher scan rates (5 mV s^{-1} and 10 mV s^{-1}). At any given potential, both the ellipsometrically measured and coulometrically estimated film thicknesses decrease with increasing scan rate i.e. higher scan rates result in thinner surface films.

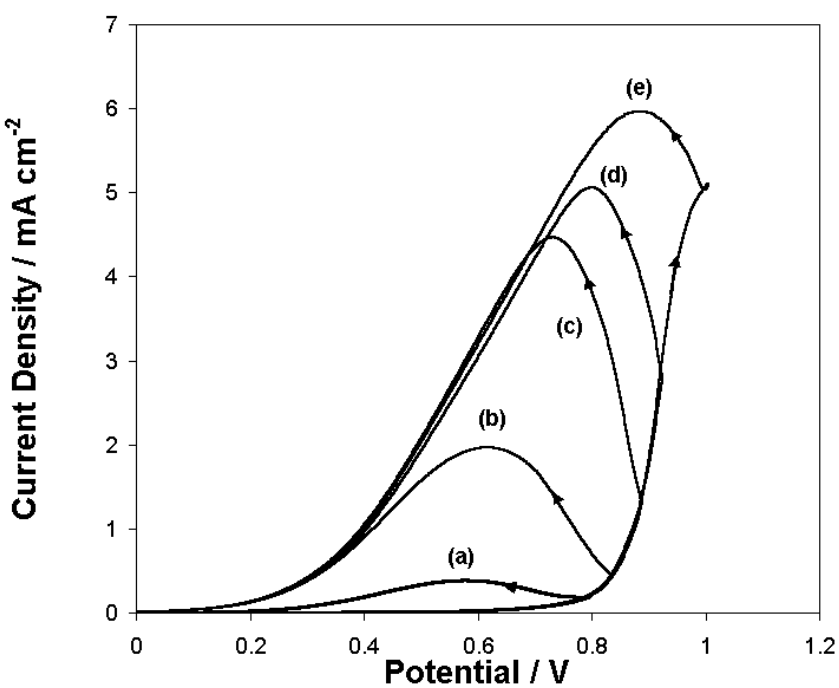

Fig. 4 *Cyclic voltammograms of InP electrodes in 1 mol dm^{-3} KOH from 0.0V to (a) 0.80 V, (b) 0.85 V, (c) 0.9 V, (d) 0.925 V and (e) 1.00 V at a scan rate of 2.5 mV s^{-1}.*

A series of cyclic voltammograms of InP electrodes in 1 mol dm^{-3} KOH from 0 V to upper potentials ranging from 0.8 V to 1.0 V at 2.5 mV s^{-1} is shown in Fig. 4.. It can be seen that the current densities on the reverse scan are greater at every value of potential than the corresponding current density values on the forward scan. A current peak is also observed on each reverse scan, similar to that observed for cyclic voltammograms of InP electrodes in 5 mol dm^{-3} KOH.[26] It was observed that cyclic potential sweeps with upper potential limits less than ~0.6 V show no pronounced peak on the reverse scan.

Ellipsometric measurements of film thickness were also made on InP electrodes which had been subjected to cyclic potential sweeps, *i.e.* after the InP sample was anodized at a scan rate of 2.5 mV s^{-1} to an upper potential of 0.88 V and stopped at various positions along the reverse sweep. The thickness of the resulting films was measured by spectroscopic ellipsometry as described above. The resulting thicknesses, plotted as a function of the final potential, are shown in Fig. 5. The corresponding thicknesses obtained during a forward linear sweep from 0 V to 1.2 V are also shown in Fig. 5 as well as the forward and reverse current curves.

As discussed earlier, it is clear that above 0.9 V in forward potential sweeps there is considerable thickening of the surface film as the potential is increased. The film continues to thicken after the current peaks at 1.03 V. However in the case of the reverse sweeps, this is not the case. When the potential is initially reversed, the film is observed

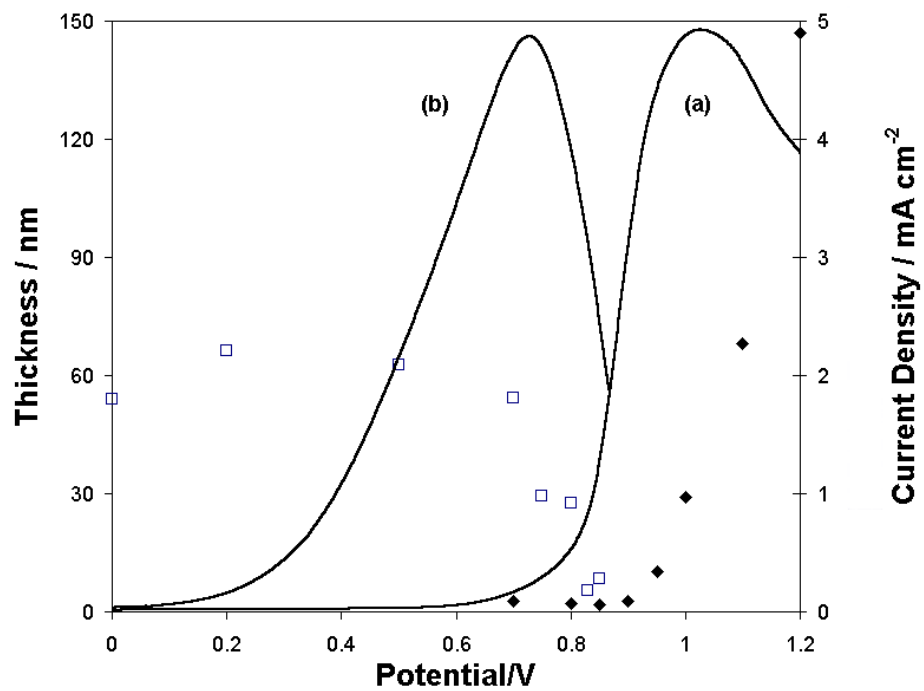

Fig. 5 *(a) linear sweep voltammogram from 0.0V to 1.20 V and (b) and cyclic voltammogram from 0.0 V to 0.88 V of InP electrode in 1 mol dm^{-3} KOH, at a scan rate of 2.5 mV s^{-1} (—). Values of film thickness measured ellipsometrically at various potentials along the forward and reverse curves are also shown (squares [□] and diamonds [♦] respectively). The lower limit of the potential sweeps was 0.0 V (SCE).*

to thicken in the same manner as on the forward sweep until the current reaches its maximum at 0.73 V. However after the current maximum we observe no significant thickening of the film in this case.

Atomic Force Microscopy

AFM was used to investigate the topography of InP electrodes which had been subjected to a potential sweep at 10 mV s^{-1} from 0.0 V to a series of upper potentials between 0.7 V and 1.1 V. Typical AFM images obtained are shown in Fig. 6. The image in Fig. 6a, which corresponds to a potential of 0.7 V, shows a rougher surface than the image in Fig. 6b, which corresponds to a potential of 1.1 V. Analysis of these images yields values of root-mean-square (*rms*) roughness of 4.4 nm and 0.5 nm respectively.

Similar AFM images were acquired for various values of upper potential from 0.7 V to 1.1 V and the *rms* roughness was estimated in each case. The resulting values are plotted against potential in Fig. 7. Clearly the roughness decreases by an order of magnitude as

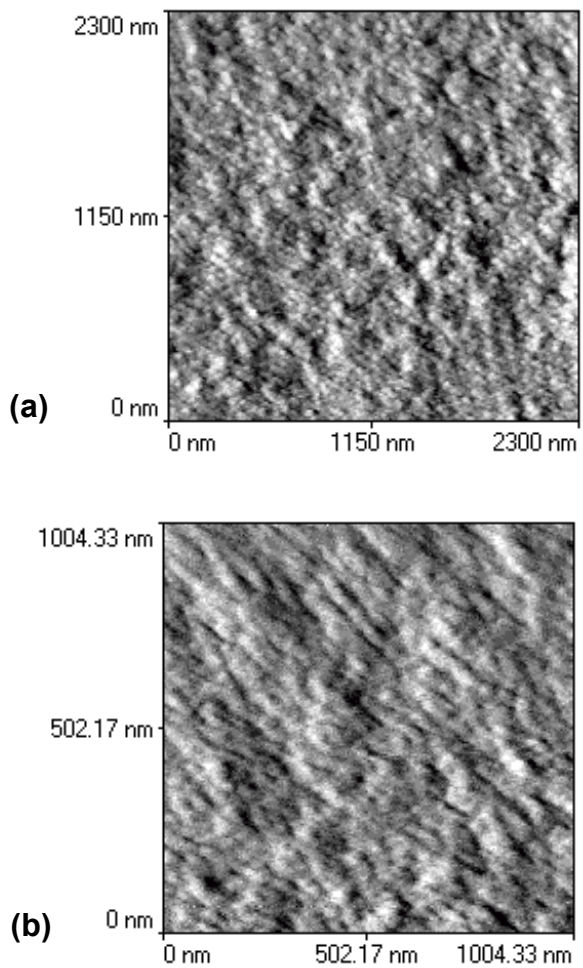

Fig. 6 *AFM images showing the InP surface topography after potential sweep anodization from 0.0 V to (a) 0.7 V (SCE) and (b) 1.1 V (SCE) in 1 mol dm^{-3} KOH at a scan rate of 10 mV s^{-1}.*

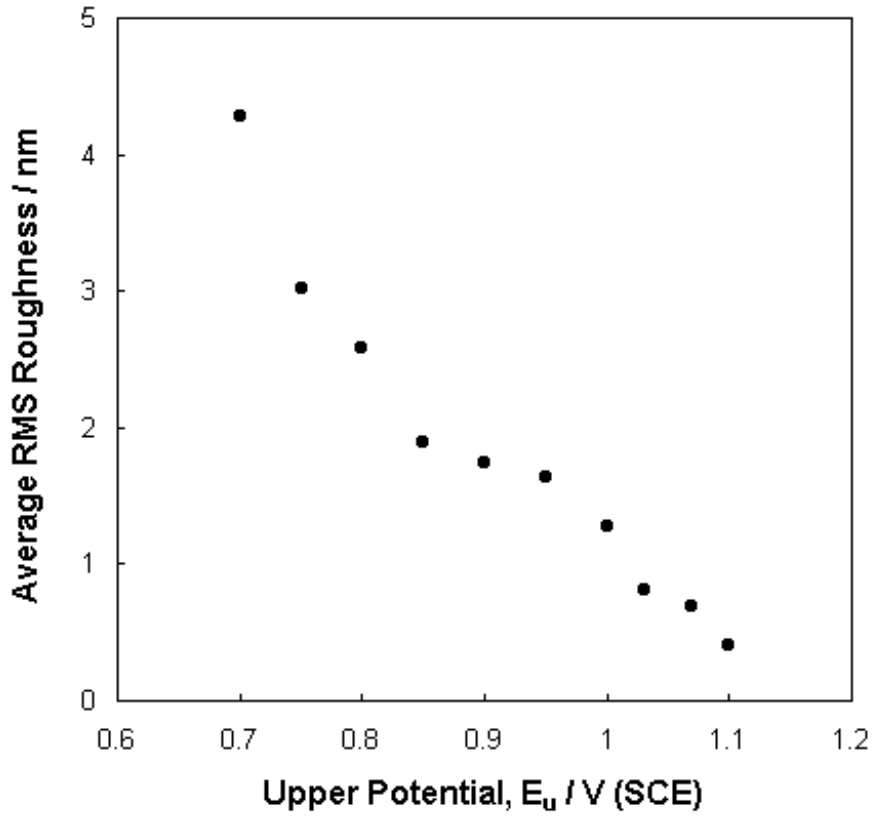

Fig. *7 Variation of the rms surface roughness for anodic films grown under potential sweep anodization in 1 mol dm^{-3} KOH at a scan rate of 10 mV s^{-1} as a function of the upper potential limit of the potential sweep. Three different areas of each sample were analyzed.*

the potential is increased from 0.7 V to 1.1 V (and the current correspondingly increases). This decrease in surface roughness corresponds to an increase in anodic film thickness as shown in Fig. 3. It is suggested that the rougher surface (such as that in Fig. 6a) at lower potential corresponds to a nucleation phase of film growth and as the film grows the nuclei coalesce and the surface becomes smoother (as exemplified by Fig. 6b).

Composition of Surface Films

Electron diffraction and x-ray photoelectron spectroscopy (XPS) were employed to identify the composition of the films. The (011) projection electron diffraction pattern shown in Fig. 8 is a selected area diffraction pattern of a thin, compact film grown under similar conditions to those described for Fig. 2. Analysis of the ring spacing shows that the anodic reaction product is In_2O_3: the diameter of the ring (from the point of maximum

intensity) corresponds to the *'d'* spacing for In_2O_3. XPS analysis of films formed under similar conditions showed negligible amounts of P (in contrast with native surface films on as-received InP which showed significant P, probably as $InPO_4$) and indicated that the anodic films consist predominantly of In_2O_3.

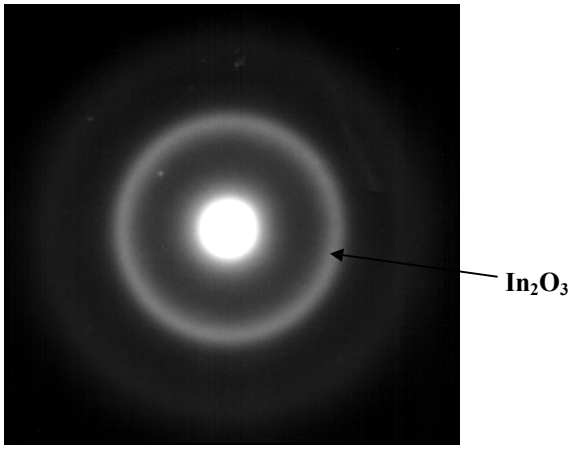

Fig. 8 *(011) projection selected area electron diffraction pattern of the anodic film formed on InP under potential sweep conditions in 1 mol dm^{-3} KOH at a scan rate of 2.5 mV s^{-1} between 0.0 and 1.0 V (SCE).*

CONCLUSIONS

The anodic processes on InP in 1 mol dm^{-1} KOH are remarkably different to those at higher concentrations (2-5 mol dm^{-1}) where a porous InP layer has been previously reported. Linear sweep anodization in 1 mol dm^{-1} KOH results in the formation of a thin compact surface film at lower potentials that thickens as the potential is increased. A peak is observed on the anodic current-voltage curve. Ellipsometric measurements show that this film increases in thickness with increasing potential but the observed thickness values are significantly less than the corresponding coulometrically estimated values. This indicates that much of the charge passed is not involved in the formation of a surface film but presumably in the formation of soluble anodic reaction products. Cyclic voltammograms show that a current peak is also observed on the reverse sweep and ellipsometric measurements show that the anodic film thickness also increases during the reverse sweep until the peak potential is reached. AFM investigation shows that the surface becomes smoother as the potential is increased. This is attributed to the formation of nuclei at lower potentials, which coalesce as the layer becomes thicker. Electron diffraction and XPS analysis show that the surface film is predominantly In_2O_3 with no evidence of $InPO_4$.

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