

An electrochemical route to GaSb thin films

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An electrochemical method for the preparation of GaSb polycrystalline thin films is presented involving sequential deposition of Sb and Ga films (from an acid SbCl_3 solution and an alkaline GaCl_3 solution respectively) and a mild thermal annealing. The annealed deposits were characterized by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis (EDAX) and secondary ion mass spectrometry. An alternative approach based on the simultaneous deposition of Sb and Ga was unsuccessful.

1. Introduction

Semiconducting III-V compounds are of great interest because of their use in the production of devices such as solar cells and sensors. When thin films of amorphous or polycrystalline semiconductors are needed, inexpensive electrochemical deposition methods may offer a viable alternative to the widely employed CVD, PACVD and sputtering techniques [1].

Many examples found in the literature concern the preparation of semiconducting chalcogenides, carried out either anodically or cathodically. Anodic synthesis of various sulphides was performed by oxidizing S^{2-} on the appropriate anodes [2-5]. This method is a straightforward one, but control of the compound stoichiometry is rather difficult. The general rules governing alloy electrodeposition hold for the cathodic synthesis, in other words the process may be successful only when electrodeposition of the components occurs at comparable rates. The simultaneous discharge of two or more ions is particularly difficult to achieve when their standard potentials are much different. However, the proximity of the standard potentials is not an absolute requirement since many other factors play a major role: ion activity in solution, cathodic overpotential, use of complexing agents and/or surfactants, activity of the metals in the alloy [6]. Binary (e.g. CdSe [7], CdTe [8, 9], Sn_{1-x}Se [10]) and ternary chalcogenides (e.g. CuInSe_2 [11]) were successfully prepared by codeposition. Various metal chalcogenides were also obtained by cathodic deposition from non-aqueous solutions containing a metal salt and molecular chalcogen [12, 13].

Less common are the examples of cathodically synthesized III-V semiconductors: InSb was obtained by codeposition from sulphate electrolytes [14, 15]; according to Sadana and Singh [15] complexation of the metal ions by citrate brings the reduction potentials of Sb and In close to each other, thus allowing codeposition in spite of large difference in the standard potentials. GaSb was deposited from a non-aqueous (glycerol) medium [16, 17].

An entirely different electrochemical approach to the synthesis of semiconducting alloys involves electrodeposition of precisely controlled amounts of the individual components as successive layers followed by thermal annealing which induces diffusion and reaction to the desired compound. CuInSe_2 was prepared by this method or by annealing a two-layer deposit of Cu and In in a H_2Se atmosphere [18]. CuInS_2 was also prepared in a similar way, the annealing being performed in an environment where H_2S was electrochemically generated [19]. The multilayer approach is claimed to be fairly general.

In the present paper we describe an investigation aimed at synthesizing thin films of GaSb by exploring the two alternative electrochemical strategies of simultaneous and sequential deposition of Sb and Ga. The electrodeposition of both pure metals (for Sb see [17, 20], for Ga [21-24]) and their anodic dissolution (for Sb see [25, 26], for Ga [27-30]) are well documented in the literature.

2. Experimental details

2.1. Substrates and electrodes

Nickel-plated Cu sheets were chosen as substrates for the preparation of GaSb films. The copper sheets ($2-3\text{ cm}^2$) were carefully degreased and rinsed with acetone followed by air-drying. Then, Ni films approximately $5\text{ }\mu\text{m}$ thick were galvanostatically deposited from a Watts-type bath of the following composition: 1.1 M NiSO_4 , 0.5 M NH_4Cl , 0.5 M H_3BO_3 and NH_4OH (pH 5.9). For some experiments, nickel (99.99%) and antimony (99.998%, Johnson Matthey) discs mounted on brass and held in a tightly fitting PTFE sheath were used as either stationary or rotating working electrodes. A carbon paste GaSb electrode was prepared by intimately mixing finely powdered commercial GaSb (1%), pyrolytic graphite powder and silicon oil (550, Carlo Erba) as the binder liquid and filling a glass tube with that paste [31].

2.2. Cells

A conventional two-compartment cell with either a platinum spiral or a platinum gauze counter-electrode and a saturated calomel reference electrode (SCE) mounted in a side arm with a Luggin capillary was used for antimony deposition and linear sweep voltammetric measurements. A similar cell modified by inserting a glass tube (0.6 cm bore dia.) through a central hole in the bottom of the cell was also used for Ga deposition. The tube was connected with a peristaltic pump which caused a continuous flow of electrolyte on the surface of the working electrode.

2.3. Chemicals

GaCl₃ (Alfa, 99.999%), SbCl₃ (Fluka, puriss.), GaSb (Johnson Matthey, 99.9999%) and all other chemicals were commercially available and used as received.

2.4. Electrodeposition baths and deposition procedures

Antimony was deposited according to a literature procedure [20] from a sulphate-chloride bath of the following composition: 0.3 M SbCl₃, 1.6 M H₂SO₄, 1.7 M HCl. The electrodeposition was performed potentiostatically at -0.25 V (with respect to SCE) for a time sufficiently long to obtain the desired thickness of the film. When a thickness greater than ~20 μm was desired, in order to avoid cracks and detaching of the deposit, a periodic (5 s) switching of the working potential from -0.25 V to the rest potential (-0.15 V) was needed. Gallium was potentiostatically deposited from 5 M KOH solutions containing GaCl₃ under conditions which will be described later. All depositions were carried out at room temperature.

2.5. Instrumentation

A computer-driven Solartron-Schlumberger 1286 Electrochemical Interface, a Hewlett-Packard 7090A digital plotter and an AMEL Mod. 731 digital coulometer were used for electrochemical deposition and linear sweep voltammetric analysis. Secondary ion mass spectrometry (SIMS) measurements were obtained by a quadrupolar home-built secondary ion mass spectrometer [32]. X-ray diffraction (XRD) data were obtained with a Philips PW 1050/81 diffractometer controlled by a PW 1710 unit. The Ni-filtered CuKα radiation was used. Scanning electron micrographs (SEM) were taken with a Cambridge Stereoscan model 250 microscope which also allowed X-ray energy dispersive analysis (EG&G ORTEC).

3. Results and discussion

3.1. Preliminary observations

Simultaneous electrodeposition of Sb and Ga was attempted under experimental conditions which

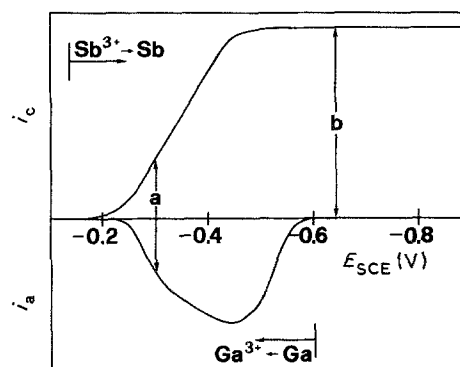


Fig. 1. Comparison of the linear sweep voltammograms of Sb deposition onto Ni (from a 0.3 M SbCl₃, 1.6 M H₂SO₄, 1.7 M HCl solution) and Ga stripping from Ni (in the same solution).

should favour the reduction of the less noble metal, that is, by using solutions containing excess Ga ions and complexing agents for Sb ions (e.g. 0.15 M Ga³⁺, 0.05 M Sb³⁺, 0.1 M citrate, pH ~ 14). Nevertheless, pure Sb was obtained, since the large difference in the standard potentials of Sb ($E_{\text{Sb}^{3+}/\text{Sb}^0}^0 = 0.212 \text{ V, SCE}$) and Ga ($E_{\text{Ga}^{3+}/\text{Ga}^0}^0 = -0.529 \text{ V, SCE}$) could not be compensated.

Therefore, we had to turn to sequential deposition of two metal layers, followed by thermal annealing to force their interdiffusion and reaction. Even with such a strategy, the large difference in the reduction potentials of Ga and Sb limits the number of experimental approaches which can be tested. Thus, the sequence - Ga deposition, Sb deposition, annealing - was unsuccessful since Ga, deposited onto Ni as the first layer from 5 M KOH containing GaCl₃, anodically dissolves at $E \geq -0.6 \text{ V}$: the attempted deposition of Sb at these potentials results in Ga displacement (Fig. 1, situation a). At $E < -0.6 \text{ V}$, Sb can indeed be deposited onto cathodically protected Ga layers but, the reaction being under diffusion control, a dendritic inhomogeneous and poorly adherent deposit is formed (Fig. 1, situation b).

These difficulties do not exist when the nobler metal is deposited first (sequence: Sb deposition, Ga deposition, annealing). However, it must be noted that Sb is converted to SbH₃ when polarized at very negative potentials [33]. We measured the loss of Sb due to SbH₃ formation by polarizing a 500 nm thick Sb film at various potentials for 100 seconds in a 5 M KOH solution and found it to be <3% at -1.85 V but >75% at -2.1 V. Therefore, such a degradative pathway of Sb imposes a lower potential limit for Ga deposition.

3.2. Gallium deposition onto Sb

Ga deposition onto an Sb rotating disc electrode from 5 M KOH was studied as a function of potential, deposition time, GaO₃³⁻ concentration and ω (the rotation rate of the electrode).

Since Ga deposition occurs at more negative potentials than H₂ evolution, strongly basic electrolytes (5 M KOH) were used, where Ga was present as GaO₃³⁻,

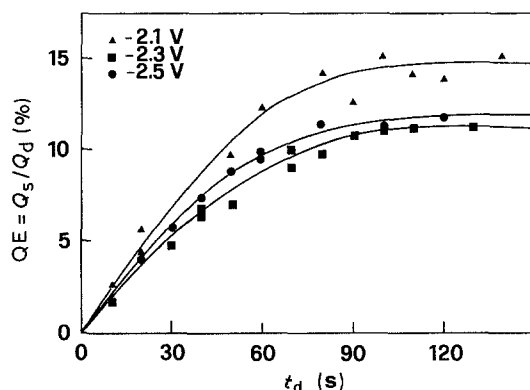


Fig. 2. Dependence of coulombic efficiency of Ga deposition onto Sb, on the electrolysis duration. Solution composition: 0.22 M GaCl_3 , 5 M KOH.

in order to improve the coulombic efficiency of the process. Nevertheless, extensive H_2 evolution always paralleled Ga deposition, the coulombic efficiency of which is far from 100% and may be determined as the ratio between the charge spent for stripping Ga (Q_s) and the total charge transferred during deposition (Q_d). The coulombic efficiency thus obtained ($\text{QE} = Q_s/Q_d$) is a value averaged over the duration of the electrolysis (t_d) and was found to increase with t_d throughout 60–90 s becoming eventually constant, Fig. 2. The average current of Ga deposition ($i_{\text{Ga}} = Q_s/t_d$) was found to vary with t_d in the same way, Fig. 3, while the total current ($i_{\text{Ga}} + i_{\text{H}}$) remained fairly constant, so that a more favourable $i_{\text{Ga}}/i_{\text{H}}$ was established while Sb was progressively coated by Ga.

The dependences of i_{Ga} and QE on potential (Figs 4 and 5) were reconstructed on the basis of Q_d and Q_s data measured for $t_d = 30$ s. GaO_3^{3-} reduction starts to occur at $E = -1.8$ V (i.e. in a potential range slightly more cathodic than for Ga deposition onto Cu [23, 24]) and becomes diffusion controlled at potentials < -2.7 V. QE is maximum between -1.8 and -2.0 V (where it reaches 25% for a 0.22 M GaO_3^{3-} concentration) and decreases substantially at more negative potentials. Rate limiting mass transfer is most likely responsible for the QE drop observed at $E < -2.0$ V for both concentrations tested. Predictably, higher GaO_3^{3-} concentrations improved Ga deposition efficiency.

The effect of mass transfer was assessed by using a

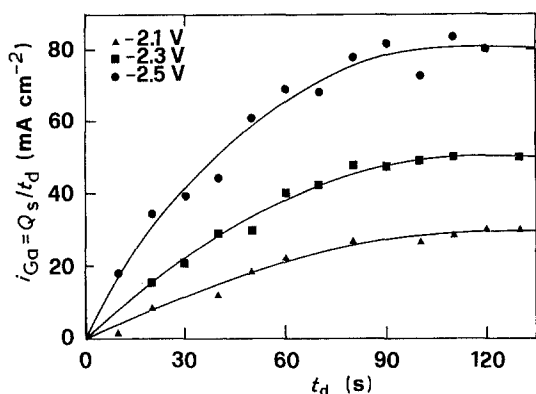


Fig. 3. Dependence of average current of Ga deposition onto Sb on the electrolysis duration. Solution composition as for Fig. 2.

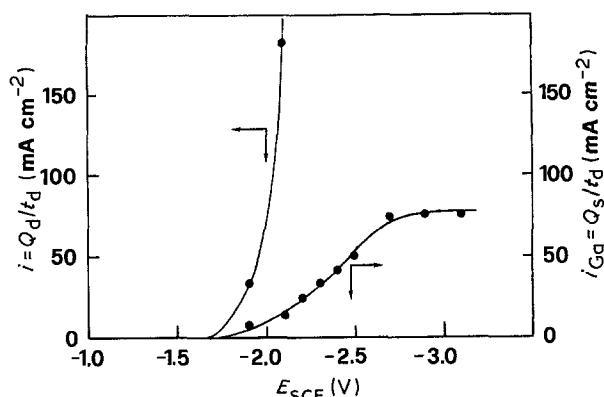


Fig. 4. Dependence of average total and gallium deposition currents on the electrolysis potential; electrolysis duration, 30 s; solution composition as for Fig. 2.

rotating disc electrode and measuring i_{Ga} and QE as a function of ω . The results obtained at $E = -2.1$ V are shown in Fig. 6 (a and b) for which a 'classical' $\omega^{1/2}$ abscissa scale was chosen. Between 200 and 2000 rpm both i_{Ga} and QE increase with ω ; the limiting values attained at high ω (> 2000 rpm) suggest that mass transfer is made fast enough that, at this potential, the kinetics of charge transfer becomes rate determining. At low ω both i_{Ga} and QE become roughly constant, probably because of the concurrent H_2 evolution reaction: bubble formation induces local stirring of the solution, thus enhancing the rate of mass transfer beyond that determined by electrode rotation. We have not tried to calculate the diffusion coefficient of GaO_3^{3-} from the data in Fig. 6 because of the shape of the diagrams and the fact that i_{Ga} is not a steady-state current but only an average value of a time dependent quantity.

3.3. Preparation and characterization of GaSb thin films

Sb layers were prepared from the solution described in the experimental section with a 100% coulombic efficiency [20].

The data reported in the two previous sections allowed us to choose experimental conditions for Ga deposition onto Sb thin layers. Fortunately, a potential window exists where QE is fairly high and Sb

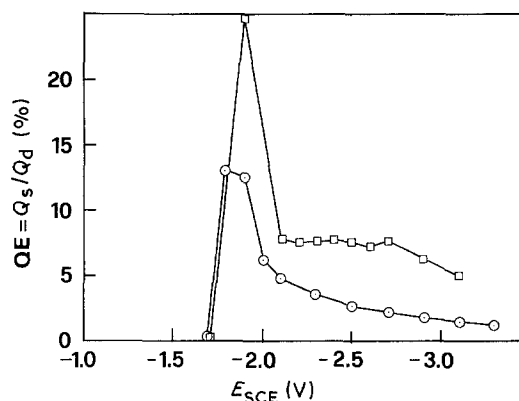


Fig. 5. Dependence of coulombic efficiency of gallium deposition on the electrolysis potential; electrolysis duration, 30 s; solution composition: 0.11 M (O) or 0.22 M (\square) GaCl_3 , 5 M KOH.

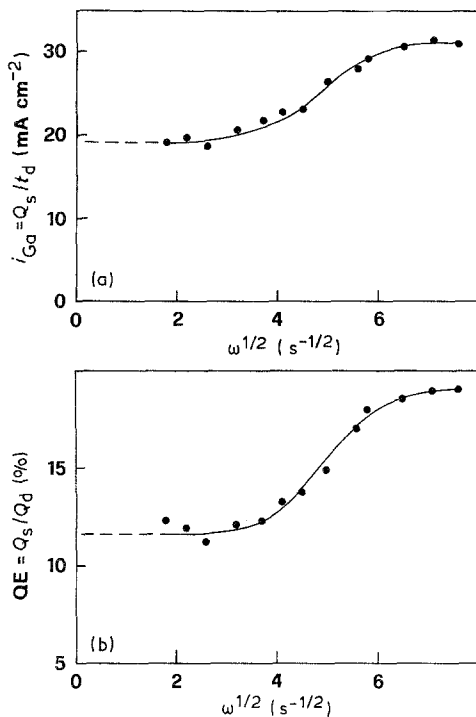


Fig. 6. Dependence of (a) average current and (b) coulombic efficiency of gallium deposition on electrode rotation rate; electrolysis potential, -2.1 V; electrolysis duration, 100 s; solution composition as in Fig. 2.

cathodic degradation (conversion to SbH_3) is negligible. Therefore we carried out Ga deposition from 0.3 M $\text{GaCl}_3 + 5$ M KOH solutions at -1.85 V for various durations in order to obtain the desired film thickness which could be controlled since QE was known. Due to the increase in QE with forced convection, we chose to use a peristaltic pump able to force a flow of electrolyte tangential to the electrode surface. A beneficial side effect of such a forced flow was the efficient removal of H_2 bubbles which otherwise would induce defects in the Ga layer if sticking to the electrode. After deposition of both Sb and Ga the two-layer coated samples were submitted to annealing under inert atmosphere, generally at 100°C for 4 h.

Typical stripping voltammograms of individual metal layers, i.e. Ga (from an Sb substrate) and Sb (from a Ni substrate), obtained in 5 M KOH are compared in Fig. 7 with the one recorded in the same medium on a crude, as-deposited two-layer sample. The stripping peak of Ga in Fig. 7a (---) at $E = -1.28$ V as well as the shoulder at more positive potential correspond to those previously observed by Dorin and Frazer [24] for Ga layers on Cu. The anodic peak at $E = -0.77$ V in Fig. 7a (---) corresponds to Sb dissolution as SbO_2^- . Since stripping charges matched the deposition ones over a wide range of film thickness, the expectation was confirmed that no anodic passivation of Sb occurs under conditions of extreme basicity. The peak at -0.92 V only appeared when stripping followed polarization of the Sb film at -1.85 V for at least 1000 s in a 5 M KOH solution (that is, nearly the same conditions for gallium deposition). The stripping voltammogram of the two-layer sample (Fig. 7b) shows main peaks (at -1.29 and

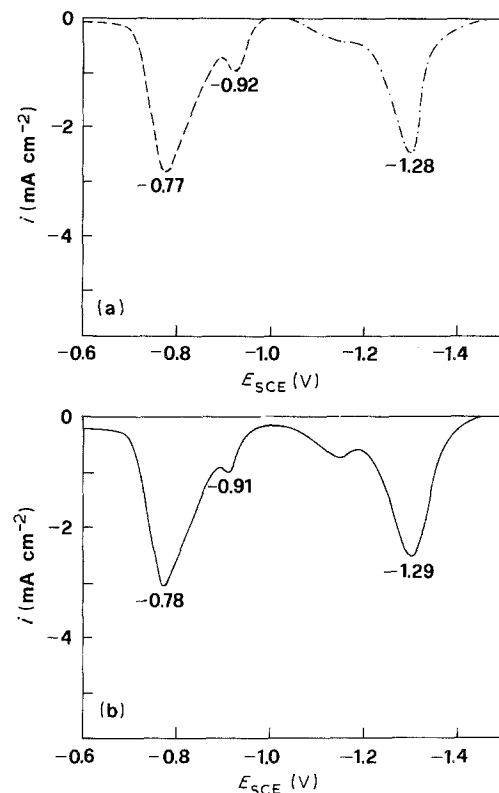


Fig. 7. Stripping voltammograms of (a) individual metal layers (Ga: ---, Sb: -.-) and (b) of an as-deposited two-layer sample. Stripping solution: 5 M KOH , potential scan rate, 1.25 mV s^{-1} .

-0.78 V) and minor features entirely corresponding to those of Fig. 7a, that is, the two layers are oxidatively dissolved independently of one another.

Thermal annealing drastically changed the stripping behaviour of a sample similar to that of Fig. 7b, see Fig. 8a. A single peak was detected at the same potential as that of Sb, but with an associated charge largely exceeding the deposition charge of Sb and corresponding (within 5%) with the sum of the charges spent for depositing both Sb and Ga (the latter estimated on the basis of QE). Fig. 8b shows the voltammogram of a carbon paste GaSb electrode recorded once again in 5 M KOH . A single oxidation peak is found at the same potential as for the annealed sample of Fig. 8a. The above voltammetric results strongly suggest that no compound formation occurs at room temperature during and after the Ga deposition stage and that a mild thermal annealing is able to induce interdiffusion and reaction between Sb and Ga.

In order to chemically characterize the annealed deposits, X-ray diffractograms of thick layers were recorded. As an example, the one corresponding to a 40 μm Sb + 5 μm Ga sample is shown in Fig. 9, where the peaks due at least in part to GaSb are marked with a star, all the others being due to the underlying Sb. The observed X-ray reflections are listed in Table 1 and compared with those expected for Ga, Sb and GaSb according to ASTM tables. Inspection of the peaks entirely due to GaSb (for example $d = 0.352$ and 0.184 nm) reveals that they have roughly the predicted relative intensities, minor variations being possibly explained by preferential orientation of the

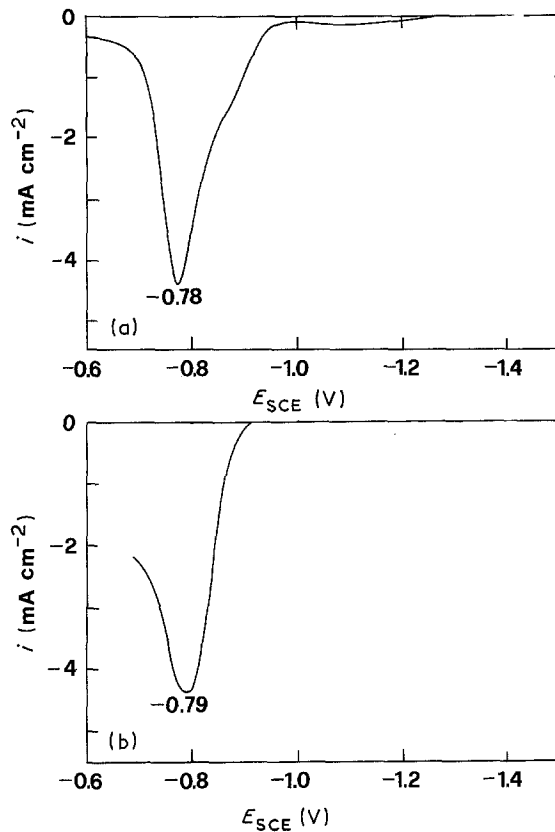


Fig. 8. Stripping voltammograms of (a) a two-layer sample after annealing under nitrogen at 100°C for 4 h and (b) a carbon paste electrode in which finely powdered commercial GaSb was dispersed. Stripping solution and potential scan rate: the same as in Fig. 7.

crystallites. No peak to be ascribed to Ga was found (note in particular the absence of the most intense Ga peak at $d = 0.295$ nm), suggesting that all Ga had reacted with excess Sb during the annealing.

Examination of annealed samples by SEM revealed

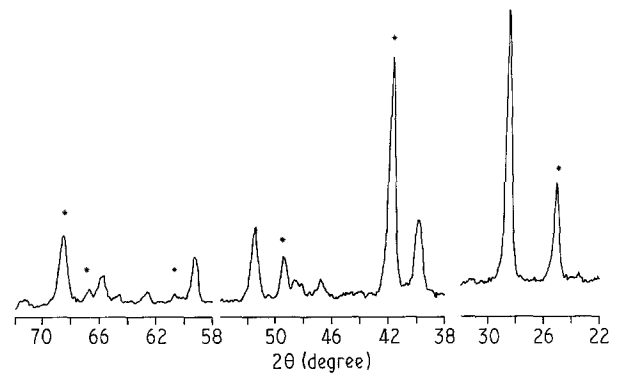


Fig. 9. X-ray diffractogram of a 40 μm Sb + 5 μm Ga sample after annealing under nitrogen at 100°C for 4 h. Ni-filtered $\text{CuK}\alpha$ radiation was used.

that most of their surface was covered by homogeneously distributed, small crystallites (typical sizes 0.1–2 μm). A few large features (up to 40 μm in diameter) were also detectable. Fig. 10 shows an EDAX spectrum recorded on an area covered by small crystallites: the main emission lines of Ga and Sb are visible and some chlorine (from the deposition electrolytes) appears to be present as impurity. The very large majority of the sample surface (small crystallites) gave spectra showing the same relative intensities as in Fig. 10, showing that the sample was chemically homogeneous, at least on the scale of the area sampled by the electron beam ($\sim 25 \mu\text{m}^2$). Stronger Ga signals were observed when an EDAX spectrum was recorded on one of the larger features present on the surface which might therefore be interpreted as due to residual unreacted Ga not detected by XRD which, sampling a much wider area, were not sensitive to local inhomogeneity.

The homogeneity of the sample in the direction

Table 1. Comparison of the X-ray diffraction peaks from Fig. 9 with those expected for Sb, GaSb and Ga according to ASTM tables

ASTM Sb 5-562			ASTM GaSb 7-215			ASTM Ga 5-601			Experimental	
d (nm)	i	hkl	d (nm)	i	hkl	d (nm)	i	hkl	d (nm)	i
0.375	25	003				0.383	28	002	missing	missing
			0.352	100	111				missing	missing
0.311	100	102	0.305	11	200				0.356	36
						0.295	100	111	0.314	100
0.225	70	014				0.293	50	102	shoulder	shoulder
0.215	56	110	0.216	67	220	0.226	60	020, 200	missing	missing
0.193	12	105							missing	missing
0.188	35	006	0.184	44	311				0.226	25
			0.177	26	022				0.216	86
			0.176	3	222				0.194	7
0.156	15	204	0.152	11	400				0.188	7
									0.186	15
0.148	13	017							0.178	27
0.144	12	025	0.140	17	331				missing	missing
0.142	63	116	0.136	3	420				0.156	16
									0.152	4
0.137	67	212							0.149	5
0.132	30	108	0.124	20	422				0.144	3
0.126	40	124							0.142	9
0.125	25	009							0.140	5
									0.137	24
									0.132	5
									0.126	9
									0.124	10

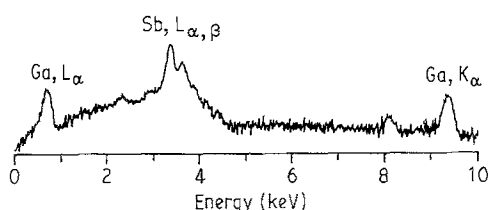


Fig. 10. EDAX spectrum relative to the same sample as in Fig. 9.

perpendicular to the electrode surface was tested by secondary ion mass spectrometry: we measured the intensities of the most significant SIMS peaks observed in the spectrum of annealed samples (which entirely matched that of commercial GaSb) while sputtering the surface with an Ar beam for several minutes. The depth profiles thus obtained are shown in Fig. 11. Although we are unable to convert the time of sputtering into depth, Fig. 11 indicates that no inhomogeneity is detected by this technique. It is interesting to note that a fairly sharp interface between Ga and Sb was detected when submitting a crude, as-deposited sample to the same sputtering experiment for a comparable time.

4. Conclusion

The above data prove that GaSb polycrystalline thin films may be prepared by sequential deposition of Sb and Ga (in this order) from aqueous solutions, followed by a mild thermal annealing. These films will be spectroscopically and physically characterized in order to assess their applicability as electronic materials. The precise control of the Ga layer thickness, necessary if a well defined Sb/Ga ratio is wanted, is made difficult by the H_2 evolution reaction paralleling Ga deposition in aqueous medium. Such a difficulty might be avoided if a suitable non-aqueous environment for Ga electrodeposition was found. To our knowledge, this is the first report of an electrochemical synthesis of a III-V semiconductor carried out by the sequential deposition method which appears suitable for extension to the preparation of other related materials.

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