Autocatalytic Deposition of Gold and Palladium onto n-GaAs in Acidic Media

G. Stremsdoerfer, H. Perrot, J. R. Martin, and P. Cléchet

Laboratoire de Physicochimie des Interfaces-UA 404-, Ecole Centrale de Lyon- B.P. 163- 69131 Ecully Cedex, France

ABSTRACT

Deposition of gold, palladium, and gold-palladium alloys is obtained with the help of acidic electroless baths of low metal content. The baths are prepared by suitably mixing separate solutions containing the reductant (hydroxylamine hydrochloride) or one of the desired cations respectively, with suitable additives. The stability of the baths with time is good and their replenishment easy to realize. Provided that a suitable choice of mixture of the three solutions is made, they allow the fabrication of multilayered heterostructures which could be fruitfully used for ohmic contact preparation onto n-GaAs without any initial activation step. The deposition mechanism of gold and palladium and the effect of adding palladium to gold is discussed.

In III-V semiconductor technology, the quality and production cost of ohmic contacts have a strong influence on the performance and price of electronic components respectively. As illustrated by the widely used Au:Ge/Ni/n-GaAs system, contacts on such materials are often made by annealing metallic films deposited onto the semiconducting substrate by conventional evaporation or sputtering physical methods (1). The nearly exclusive use which is made of these "dry" deposition methods during the manufacture of the contacts is mainly due to their versatility and their compatibility with other fabrication steps of III-V components or integrated circuits. Nevertheless, they lead to a high production cost, mainly because of the expensive and complex facilities they require. From that point of view, "wet" chemical methods of deposition, which are much simpler and cheaper, could be in some circumstances a satisfactory alternative, especially as they allow selective metallization even on nonplanar surfaces [e.g., for contact hole filling (2, 3)]. Indeed, a survey of the literature on III-V metallization shows that electroplating has sometimes been used for the preparation of ohmic contacts onto p-type InP (4, 5) and photoelectroplating onto n and p-type InP (6) but, to our knowledge, not onto GaAs. On the other hand, electroless methods, although more attractive for semiconductor technology because they do not require a rear side electrical contact, were not considered before 1985. At that time, we showed that a suitable combination of autocatalytic and displacement reactions can be used successfully in that field. We first described a process (7) in which the successive autocatalytic deposition of tin and gold, with baths proposed by Molenaar and Coumans (8) and D'asaro et al. (9), respectively, onto n-GaAs surfaces previously activated by a palladium deposit, lead to low-resistive contacts (about 2.10^{-4} Ω cm²) after heat-treatment at 420°C. Other conclusive results were published by us afterward, using either pure gold (10) or indium:gold alloys (11) on the same preactivated GaAs substrates, and by Korde and Weinketz on p-InP by deposition of a zinc-cobalt alloy (12). In the working processes described in the above-cited paper on goldbased contacts onto n-GaAs, there were three main complicating drawbacks.

I. The first arises from the strong alkalinity of the deposition baths. Positive photoresists being unstable at high pH, negative resins have to be used to generate the pattern for the specific resistance contact measurement. Stripping such resins appears to be difficult and the obtained resolution poor. Moreover, our intended metallization of InP could not be envisaged with them, as they strongly corrode this material.

II. The second results from the poor stability of the baths which all use potassium borohydride as the reductant. This lack of stability is a great handicap for industrial applications, even if some of the baths are easily recoverable (11).

III. The third is that in an alkaline medium, the catalytic activity of GaAs surfaces is very low and has to be strongly enhanced before the autocatalytic deposition of gold can proceed. As mentioned above, this enhancement is realized by the preliminary deposition of palladium, obtained by simply immersing the material in a strongly acidic solution of palladium chloride (9, 10).

The strategy we have chosen to solve these problems is based on the following three points. (i) the choice of a new reductant which can work in acidic media and whose stability over a period of time is good when stored as an aqueous solution, (ii) the use of dilute metallic ion solutions in order to decrease the kinetics of their reduction in the bulk solution while keeping the deposition rate of the metal on the catalyzed semiconductor surfaces close to a few 0.1 μ m/h. (Such a rate allows the preparation of the very thin metal layers which are required by ohmic contacts [a few 10² nm] in a reasonable length of time, even at low temperatures [<90°C]; another more concentrated bath can be used afterwards for the thickening of the contacts] and (iii) the elimination, if possible, of the activation step of GaAs in the new acidic baths because of their etching effect. As in the case of the activation solution this might lead to an oxide-free surface which could be more active for the initial step of metal deposition.

The experimental results reported here prove that these assumptions were realistic. Previous work (10) having shown that the successive deposition of palladium and gold leads to good ohmic contacts onto n-GaAs substrates, the above scheme was checked against this system, which is moreover known to give a continuous series of solid solutions (13). Codeposition of these metals can thus be envisaged which, if successful, would be a further advantage of the method.

The most important quality we require for our acidic autocatalytic baths, in addition to good stability with a lifetime longer than one month, even after the bath has been used once for 2h and then possibly replenished, is their ability to give a well-structured deposit only in the desired place (lateral resolution and selectivity), even when they are close to complete exhaustion. The physical properties of the layers obtained (adhesion, morphology, lateral uniformity...) during the deposition process and the progressive consumption of the low metallic content must obviously remain unchanged.

Experimental

Single-crystal (100) GaAs were obtained from RTC as substrates of a thickness of 300 μ m, n-doped with Si to about 10¹⁸ cm⁻³. Chemical deposition processes being sensitive to surface cleanliness, the samples were successively lapped with 6, 3, and 1 μ m diamond pastes and then thoroughly degreased with hot organic solvents using soxhlet cycles (trichloroethylene, acetone, isopropanol and methanol). The remaining native oxide layer was likely eliminated during immersion in the acidic deposition bath. We used a Teflon rotating carousel similar to that described by Okinaka *et al.* (14) and a positive photoresist resin (SHIP-LEY AZ/350) for wafer mounting.

Because they are designed to work at high temperature, the gold deposition baths proposed by Bellis and Hook-

Table I. Electroless bath composition and storage conditions. Gold deposition bath:add x ml of solution 2 to 40 ml of solution 1. Palladium bath deposition (activation step):pure solution 3. Palladium:gold alloy deposition bath:add x ml of solution 2 and y ml of solution 3 to 40 ml of solution 1.

Solution	Composition			Storage vessel		
1 (for 100 ml)	NH ₂ OH.HCl KHF ₂ KCl Citric Acid (C ₆ H ₈ O ₇ , H ₂ O)	0,416 0.937 14,912g 2,101g	(0.06 <i>M</i>) (0.12 <i>M</i>) (2 <i>M</i>) (0.1 <i>M</i>)	Polypropylene or "Teflon"		
2 (for 100 mÌ) 3 (for 900 ml)	D.1. water KAu (CN) ₂ D.I. water 0.3g PdCl ₂ dissolved in 9 ml HCl 5 ml D.I. water 864 ml glacial acetic acid 22 ml HF (40%)	0,576g	(0.02 <i>M</i>)	Glass Polypropylene or "Teflon"		

Table II. Experimental conditions for gold deposition on bare (non-Pd-activated) n-GaAs and physical characteristics of the deposits e:thickness
 of the deposits after 1h of deposition.

Type of bath	Bath composition	Temperature of deposition °C	e/µm	Appearance	Adherence	Grain size/nm
A A A	1 ml sol. 2 + 40 ml sol. 1 (C ₄ = 5.10 ⁻⁴ M)	40 60 70	0.1 0.2 0.4	yellow uniform yellow uniform yellow uniform	poor poor poor	50 60 60

essin (15) and Moskichev et al. (16) were not considered. We preferred that proposed by Dettke and Stein (17) which contains, like the palladium deposition bath used for the activation step of n-GaAs, a large concentration of fluoride ions, among other chemicals. This can be a favorable factor for the proposed preparation of a palladium:gold codeposition bath. However, Dettke's bath, as described in the patent, i.e., with a large cation concentration, appears not to be usable at the temperature indicated. After several minutes at 80°C, a yellow precipitate develops in the whole apparatus. In order to enhance its stability, we decided not to change the reductant (hydroxylamine hydrochloride) and additive concentrations (KHF2, citric acid, and KCl) but to use much lower metallic concentrations [KAu(CN)2]. The mother solutions, which are described in Table I, are stored separately and mixed in suitable proportions just before use. For the activation of a GaAs surface by the predeposition of palladium, solution 3 was used at room temperature with an immersion time of 30 min. The exchange reaction produced a palladium layer about 25 nm thick

САЦ/М 10⁻⁶ UNSTABILITY 10⁻⁶ STABILITY 10⁻⁶ 20 40 60 80 $\Theta/_{7}$

Fig. 1. Curve showing the maximal temperature at which autocatalytic deposition baths containing various concentrations of gold (Table I) can be used for 2h while remaining chemically stable, at room temperature, for one month.

after a 30 min deposition time (10). After being activated the samples were thoroughly rinsed in DI water.

Results and Discussion

Autocatalytic deposition of gold on bare (non Pd-activated)n-GaAs substrates.-The deposition baths for the autocatalytic deposition of gold in acidic media are prepared by mixing a suitable quantity of solution 2 with 40 ml of solution 1 (Table II). After a working deposition time of 2h at a fixed temperature (40°, 60°, and 70°C, respectively), the length of time during which a bath remains stable (absence of any precipitation in the bulk solution) at room temperature is represented in Fig. 1 for various gold concentrations. If deposition is performed at a temperature higher than that indicated by the curve for a given gold concentration (C_{Au}), the bath can be used again at the cost of shortening its stability at room temperature. In Fig. 2, curve 1 represents the variation with time of thickness e of a gold deposit with the baths described in Tables II and III at 40°C. As we used a 40 ml deposition bath volume, it



Fig. 2. Deposit thicknesses obtained on (100) n-GaAs substrates. Curves 1 and 2 correspond to pure gold deposits, obtained respectively on bare and Pd-activated highly-doped n-GaAs (10^{18} cm⁻³) at 40°C (bath A). Curves 3 and 4 correspond to Au:Pd codeposits obtained on the same bare substrate at 40°C and 60°C, respectively, (bath B). In the inset, symbols 1, 2, 3, and 4 are the same; curve 5 corresponds to a pure gold deposit obtained, at 40°C, with the same solution used for curves 1 and 2 on low-doped n-type (10^{16} cm⁻³) and p-type GaAs.

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Table III. Experimental conditions for Pd:Au codeposits obtained on bare (Pd nonactivated) n-GaAs substrates; e is the thickness of the deposit
after 1 h of deposition.

Type of bath number	Bath composition	Temperature of deposition °C	e/µm	Appearance	Adherence
В	1 ml sol. 2	40	0.2	yellow uniform	good
	+				
	0.1 ml of sol. 3	60	0.4	yellow uniform	very good
	40 ml sol. 1 $C_{AU} = 5.10^{-4}M$ $C_{DV} = 4.10^{-6}M$	70	0.5	yellow non uniform	good
С	1 ml sol. 2	40	0.6	red	good
	0.5 ml sol. 3	60	0.7	red	good
	$\begin{array}{c} 40 \text{ ml sol. 1} \\ \mathbf{C}_{\mathrm{AU}} = 5.10^{-4}M \\ \mathbf{C}_{\mathrm{Pd}} = 2.10^{-5}M \end{array}$	70	0.8	red	good

can be noted that a 2 µm thick gold layer can be deposited onto a 1 cm² surface before the gold content of this solution is completely exhausted. Thus, with a deposition rate of a few 0.1 μ m h⁻¹, such a bath can function for about half a day. For a deposition of 1h on bare GaAs substrates, the thickness of the deposit varies from 0.1 µm at 40°C (Fig. 2, curve 1 or Table II) to 0.4 µm at 70°C (Table II). After an initiation period of about 1h, it is clear that full coverage of the surface with gold is reached in such a way that the autocatalytic deposition of gold on gold can then freely proceed at a rate which is close to 0.1-0.2 µm/h at 40°C. The activation energy of the gold-on-gold deposition, as determined from an Arrhenius plot of the deposition rate, is close to 30 kJ mol⁻¹, a value which agrees with the usual values obtained for liquid catalytic processes. The grain size of the deposits, as determined by SEM, is about 50-60 nm. The x-ray diffraction spectrum indicates that the crystal structure of gold so deposited is similar to that obtained by vacuum deposition. The adherence of the films is low but is somewhat improved when the temperature of deposition is increased.

Autocatalytic deposition of gold on Pd-activated n-GaAs substrates .-- The mechanism of the n-GaAs Pd-activation step when realized with solution 3 at room temperature has been described elsewhere (10). The growing curve for gold deposition, using the same bath as above, is represented in Fig. 2 (curve 2). Surprisingly, the induction period is then two or three times longer than in the absence of palladium but, as expected, the deposition rate afterward reaches the same value as on bare n-GaAs at the same working temperature. We have recently observed that the electroless deposition rate of In:Au alloys in an alkaline medium, on Pd-activated n-GaAs surfaces, greatly depends on the duration of the activation step (11). A maximum is obtained after a deposition time of 5 min, which corresponds to the best catalytic activity of the dispersed Pd deposit (10). The long induction time which is obtained here for gold deposition in an acidic medium can certainly be shortened by changing the activation time. This problem, being of secondary importance, has not been considered. The morphology of the deposit is similar to that obtained without Pd-activation, but its adhesion is now very good, as previously observed (10).

Autocatalytic codeposition of gold and palladium on bare n-GaAs substrates.—As noted above, the autocatalytic and displacement deposition baths of gold and palladium being at the same time highly acidic and fluoride ion rich, the codeposition of the two metals as homogeneous solid solutions (13) might be possible with a bath prepared by mixing solutions 1, 2, and 3 in suitable proportions (Table I). As a general rule, we observed that adding palladium to the autocatalytic gold deposition bath leads to a decrease in its stability so that in the experimental conditions used here (Table III), no more than 0.5 ml of solution 3 could be added.

The advantage expected from such codeposition is to cumulate both a short activation time (as is observed on bare n-GaAs surfaces) and good adhesion of the deposit (as is obtained on Pd-treated surfaces). The composition of the two codeposition baths (B and C) used in this work is described in Table III; like the other baths, they meet the stability requirements defined in the introduction and in the caption of Fig. 1. The best adhesion of the deposit is obtained at 60°C, with a low content of palladium (4.10^{-6} M). The geometric resolution of the codeposit is fairly good, as shown in Fig. 3 by the SEM micrography in which a pattern size down to 1 µm was achieved with bath B at 60°C. At 70°C the resolution is slightly worse. Micrographs of Fig. 4 clearly show the deleterious effect of an increase in both the deposition temperature and the palladium concentration on the roughness and porosity of the deposits. In all cases, atomic absorption analyses established that the palladium concentration is low, being less than 1% by weight, which explains why the x-ray diagram of the deposit is the same as that of pure gold.

On the other hand, Fig. 2 shows that both the induction time and the deposition rate are considerably improved by the presence of palladium. With bath C, the deposition rate is about ten times greater than for gold alone at the same temperature. The measured activation energy is nearly the same as that obtained with pure gold.

Electroless deposition of palladium on bare n-GaAs.—An autocatalytic bath for palladium deposition, which was prepared by adding a small quantity if solution 3 to 40 ml of solution 1, was tested. Even at 20°C, the induction time was so short and the deposition rate so high that the corresponding growing curve could not be drawn in Fig. 1. The deposits are well structured and adherent. At a higher temperature, the adhesion quickly decreases and the layer becomes rough as a consequence of the extremely high rate of deposition which is then obtained. Other palladium

Fig. 3. SEM micrograph (\times 1000) of a Pd:Au pattern obtained by a 1h electroless deposition using bath B at 60°C (e = 0, 4 μ m). Black dots are due to room dust against which no precautions were taken during deposition.

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Fig. 4. SEM micrographs of Pd:Au films obtained on bare n-GaAs substrates after 1h deposition (×4000); (a) bath A, = 60°C, e = 0.4 μ m; (b) bath B, = 60°C. e = 0.7 μ m; (c) bath A, = 70°C, e = 0.5 μ m; (d) bath B, = 70°C, e = 0.8 μ m.

deposition baths have been already described in the literature, but their compositions are not satisfactory for our purposes (18-20).

Discussion of the experimental results.—In alkaline media, the autocatalytic deposition of gold onto untreated n-GaAs does not occur. In order for the gold deposition to proceed, the deposition of palladium is first required as a catalyst through an exchange reaction between the substrate and palladium ions (9, 10). This reaction is conducted in an acidic medium in order to prevent the precipitation of palladium hydroxide in the bulk solution and to eliminate native oxides on the surface of GaAs. At low pH, the exchange reaction, as explained elsewhere (10), can develop because the top of the valence bandedge of GaAs is favorably situated with regard to the Fermi level of the $PdCl_4^{2-}/Pd$ redox system which is then observed (Fig. 5). On the other hand, in acidic media, the autocatalytic

deposition of gold on untreated surfaces of GaAs has proved to be possible with the baths we have developed. Moreover, the induction time appears to be shorter on bare than on Pd-treated GaAs, when it is close to 1h both in acidic (Fig. 2, curve 1) and in alkaline media (21). Because of the position of the Au(CN)₂^{-/}Au Fermi level at low pH [the HCN evolution is prevented by the high stability constant of the gold cyanurate complex which is close to 10³⁹ see Ref. (22)] which is indicated in Fig. 5, the initial step for the deposition of gold cannot be a hole injection process. Two other explanations, which are not mutually exclusive, can be suggested for this observed spontaneous deposition. The first is that the catalytic activity of the surface of GaAs, which is freed of oxide traces when immersed in the solution, could be suitable for the reduction of gold ions by hydroxylamine. The second is that the autocatalytic reduction of gold ions could be initiated by the preliminary ab-

sorption of these ions, which is likely facilitated by the presence of free electrons on the surface of GaAs because of the flatness of its bands in this solution (Fig. 5). The first underlying layers of metal now being obtained by adsorption (free surface) and not by ion exchange (Pd-treated surface), the observed difference in adherence for the two kinds of gold deposits would thus be explained. The latter mechanism agrees with the experimental results presented in the inset of Fig. 2, where the initial deposition rate of gold on bare n-GaAs in an acidic medium is slower on p-doped and low-doped n-GaAs (10^{16} cm⁻³) than on highly doped (2.10¹⁸ cm⁻³) n-GaAs. As the relative position of the bandedges mainly depends on the composition of the solution, which here remains unchanged, the electron concentration is more likely to be different from one sample to the other in the bulk than at the surface. As the bulk electrons are used to refill the electronic states which are partially or fully emptied by the adsorbed ions, this replenishment is more easily accomplished with the highly n-doped samples than with the others. Moreover, as the adsorption of positive ions is always accompanied by a positive shift of the bandedges, the higher the adsorption, the greater the shift, which leads to an increase in the number of surface electrons used in the adsorption process. Both these effects account for the higher deposition rate observed on highly n-doped samples.

The higher rate of deposition which is observed for palladium than for gold proves that palladium is the best selfcatalyst of these two metals for their own deposition. Thus, the mechanism by which palladium ions are reduced in acidic media is probably first an exchange reaction, which initiates the deposition, followed by an autocatalytic process. At the same time, the very highly self-catalytic properties of palladium and the lower stability of the bath containing palladium explains why the deposition rate of



Fig. 5. Approximate energy level diagram for the GaAs/acidic aqueous interface. The indicated Fermi levels in the solution correspond to the standard situation without any correction for the true concentrations used in this work.

Pd:Au alloys (curves 3 and 4, Fig. 2) is faster than that of gold alone (curve 1, Fig. 2).

Conclusion

To conclude, it can be observed that the improvement in gold deposit resolution which is obtained through the use



Fig. 6, J-V characteristic of a Pd:Au (<1% in weight)/n-GaAs (2.10¹⁸ cm⁻³) contact after an annealing time of 2 min at several temperatures. of positive photoresists is not the only beneficial consequence of changing the *p*H of the autocatalytic deposition bath from basic to acidic. Another great advantage is the elimination of the previous Pd-activation step, admittedly at the price of a lower adherence of the deposits which, nevertheless, can be improved either by subsequent annealing, or by the addition of palladium ions in the bath. This addition also leads to a decrease in the length of the initiation step. Figure 6 proves that, as expected, annealing of Pd:Au/n-GaAs heterostructures obtained by the codeposition process described here, improved the ohmicity of the contact, even with a very low concentration of palladium (here <1% by weight). As this concentration can be easily increased by choosing a bath composition richer in palladium, it can be reasonably predicted that ohmic contacts of good quality (p_c in the $10^{-5} \Omega$ cm² range) will be obtained with this process. This prediction is supported by the results we have already obtained on similar heterostructures (10). However, the bath stability will then be doubtful.

Lastly, the realization of multilayered metallic heterostructures can be envisaged by the successive addition of small aliquots of various dilute (and thus easily exhausted) solutions containing palladium, gold, or any other autocatalytic metals, to a bulk solution containing the reductant. This can be a useful way of making refractory (Pd-based) ohmic contacts in the future.

Acknowledgments

The authors wish to thank Dr. Y. Robach and Dr. Nguyen Du for making the ellipsometric and x-ray measurements.

Manuscript submitted Nov. 16, 1987, revised manuscript received March 29, 1988. This was Paper 500 presented at the Honolulu, HI, Meeting of the Society, Oct. 18-23, 1987.

Laboratoire de Physicochimie des Interfaces assisted in meeting the publication costs of this article.

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Transport of Nickel and Oxygen during the Oxidation of Nickel and Dilute Nickel/Chromium Alloy

A. Atkinson and D. W. Smart¹

Materials Development Division, Building 552, Harwell Laboratory, Didcot, Oxfordshire, OX11 0RA, England

ABSTRACT

NiO films have been grown on high-purity Ni and Ni 0.1 weight percent (w/o) Cr alloy, at 700°C and 0.21 bar, by sequential oxidation in ${}^{16}O_2$ and ${}^{18}O_2$. The distributions of oxygen, Ni, and Cr isotopes in the films were analyzed using SIMS. For both materials, the rate controlling transport process was found to be the outward diffusion of Ni through the NiO. Inward oxygen gas transport also occurs and is responsible for the growth of new oxide within the films and for the growth of the inner layer of the well-developed duplex films which grow on the alloy. A mechanism whereby oxygen gas penetrates the films through fissures to form new oxide in available space is proposed to explain the observations and the growth of duplex films.

The protective properties of oxide films formed by oxidation of metals depend on the transport of reactants (metal and oxygen) through the film and the structure of the film (including the microstructure). In general, the transport properties and structure of the oxide film are inter-related. In some cases, this relationship is relatively straightforward; for example, the oxidation of high-purity Co or Ni at high temperatures, when the classical singlelayer, single-phase compact oxide film grows by outward diffusion of metal ions through the oxide lattice. At the other extreme, the relationship is extremely complicated; for example, the oxidation of a multicomponent alloy in mixed gases at intermediate temperatures. The complicating factors include multiphase, multilayered, doped oxides containing voids, dislocations, and grain boundaries as additional potential routes for transport through the oxide.

Between these two extremes is an important class of oxide film microstructures known as duplex films (or scales). Duplex films are formed under a wide variety of conditions on a large number of metal substrates. They can form on high-purity metals as well as on alloys. On high-purity metals, the inner and outer layers of the duplex film are distinguishable by their different grain size. The outer layer usually has a columnar structure, and the inner layer has an equiaxed structure of much finer grain size. The thickness of the inner layer, as a fraction of the total layer thickness, appears to depend on the system and the experimental conditions. However, the inner layer thickness never exceeds the thickness of metal converted to oxide (*i.e.*, when the inner-layer/outer-layer boundary coincides with the position of the original metal surface). When duplex films form on dilute alloys, the inner-layer/ outer-layer boundary usually coincides with the position of original alloy surface, and the alloying elements are preferentially located in the inner layer (provided that the alloying elements have low mobility in the oxide).

The transport processes which occur during duplex film growth have been studied using isotopically labeled oxygen tracers in a number of systems. The results of these experiments and their interpretation have recently been reviewed by Atkinson (1). The experiments have shown that the outer layer of the duplex structure (and the whole film, if it is a single layer of the same oxide) grows by outward diffusion of metal ions. The inner layer, on the other hand, grows by inward transport of oxygen. The mechanism by which the oxygen moves through the film is not clear, but

¹ On leave from Department of Metallurgy and Materials Science, Imperial College of Science and Technology, London.

is generally believed to be as gas molecules along open porous channels traversing the oxide.

The level of understanding of this phenomenon leaves much to be desired. In particular, we have no rationalization of the conditions under which duplex films form, nor the processes which create and maintain the pathways for inward oxygen transport. The purpose of the work described here was to investigate the mobility of oxygen during the growth of single-layer and duplex films of NiO, on high-purity Ni and dilute Ni-Cr alloy, respectively, using modern techniques of secondary ion mass spectroscopy (SIMS) for the location of isotopically labeled oxygen tracer.

Experiments

Specimen preparation .-- The metal specimens were square coupons with nominal dimensions, $10 \times 10 \times 0.5$ mm, of either high-purity Ni or a nominal Ni 0.1% (by weight) Cr alloy. The Ni was Puratronic grade (Johnson Matthey Chemicals, Limited, Royston) and the maximum impurity level for any one element was found to be no more than a few ppm, with the total impurity content no greater than 30 ppm. The Ni 0.1% Cr coupons were made by alloying Cr with the high-purity Ni. Elemental analysis of this alloy revealed a Cr content of 840 ppm, with the other major impurity being 40 ppm Fe.

To ensure reproducibility in the subsequent oxidations, a standard specimen preparation procedure was followed. The coupons were first mechanically polished on both faces to a mirror finish using, 1 µm diamond on a plastic lap. Each coupon was then annealed for 1h at 900°C in a flowing stream of wet gas consisting of 30% H₂ and 70% N₂. Optical microscopy revealed that at this stage the grain size was about 100 µm. Each face of the coupon was then lightly repolished on the 1 µm lap for 5 min. This second polishing removed any surface oxide and etching topography and also introduced some mechanical damage. This damage is experimentally beneficial since it promotes the growth of a film which is uniform over the whole surface, rather than one with different thicknesses over different metal grains. Each coupon was finally washed in acetone and then distilled water in an ultrasonic bath.

Sequential oxidation in ${}^{16}O_2/{}^{18}O_2$.—The apparatus which was used is shown schematically in Fig. 1. It consists of a fused silica furnace tube and stainless steel gas handling facilities and could be evacuated to a residual pressure of about 5 \times 10^{-8} mbar. The oxygen gases were contained in zeolite-filled sorption pumps. The nominally "16O2" gas was high-purity oxygen of normal isotopic composition