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STUDY OF IONIC MOVEMENTS DURING ANODIC OXIDATION OF NITROGEN-IMPLANTED ALUMINIUM

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In recent years there has been a considerable interest in synthetizing aluminium nitrides by ion implantation in order to modify the tribological properties of aluminium. The growth of an oxide layer by anodic process on these synthetized aluminium nitrides gives an interesting oxide-on-semiconductor material with surprising dynamic and decorative properties [1]. During the anodic oxidation, ionic movements are involved in the near-surface region of the aluminium material; these ionic movements have been studied by Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) on thin aluminium foils (7000 Å) preimplanted with nitrogen and post-oxidized in an ammonium pentaborate solution. The growth of the oxide layer is reduced when the aluminium is preimplanted with nitrogen: the speed of oxidation depends on the implantation conditions (energy and fluence). Moreover, the aluminium nitride can be dissolved when all metallic aluminium staying between the surface and the AlN are consumed by the anodic process.

1. Introduction

Anodic oxidation of aluminium has been largely investigated by many authors [2–4]. The oxide layer formed by the anodic oxidation process has properties which can be used for industrial applications such as electronical devices, decorative and protective coatings.

On the other hand, aluminium nitride, which can be synthetized by ion implantation [5], is of potential interest due to its mechanical, electrical and optical properties. Anodic oxidation of such a system is of great interest because it allows us to study the resistance of an aluminium nitride layer formed by implantation in corrosive surroundings. It has been shown recently that anodic oxidation performed on aluminium implanted with nitrogen leads to the formation of an oxide layer on synthetized aluminium nitride with surprising dynamic and decorative properties [1].

The aim of this work is to study the evolution of the oxide and aluminium nitride layers in more detail in order to try to explain the ionic movements during the oxidation. Thin aluminium samples previously bombarded with nitrogen have been oxidized. The depth distributions of the light elements (B, N, O, Al) were investigated by Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) during the anodic oxidation process.

* Holder of an doctoral fellowship of IRSIA.

2. Experimental details

2.1. Sample preparation

In order to easily detect the light elements with the RBS technique, we have prepared thin self-supported aluminium foils (7000 Å) for this study. To avoid heat damaging of the film during implantation, it is necessary to have a backing for the substrate. Since copper is a good heat conductor, and since it is possible to dissolve copper without dissolving the aluminium, we have found it a suitable material for backing.

7000 Å Al was evaporated onto 0.5 mm thick and 12 mm diameter Cu samples, and the aluminium was implanted with 100 keV $^{15}N_2^+$ to different doses (10^{17}, 5×10^{17} and 10^{18} N^+/cm^2) with the 600 kV implanter of Århus. The copper was dissolved in a 7N HNO_3 solution and the aluminium foil was mounted on an aluminium frame.

The oxidation was carried out at different voltages – from 50 to 295 V – with an ammonium pentaborate solution ($(NH_4)_2B_{10}O_{12}$) with a concentration of 50 g/l and a pH of 7.65 and at a current of 20 mA/cm^2. A drop of this solution was placed on the sample, contained by a glue ring in order to avoid oxidation of the back and of the unimplanted area. Anodic contact was made outside the ring of glue, while the aluminium cathode was placed in the electrolyte.

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2.2. Depth profile measurements

The nitrogen distributions were measured using the well-known $^{15}N(p, \alpha\gamma)^{12}C$ nuclear resonant reaction which presents a very narrow resonance (with a width of less than 300 eV) at $E_p = 429$ keV. The proton beam was produced by the 2.5 MV Van de Graaff accelerator in Namur, and the depth profiles were obtained by varying the proton energy and counting the γ-rays with a 4 in. × 4 in. NaI scintillator [6].

The boron depth profile was performed by using the $^{11}B(p, \alpha_0)^8Be$ resonant nuclear reaction at an energy of 165 keV [7]. The alpha particles were detected with a passivated implanted planar silicon detector (PIPS) at a backward angle. In order to stop the backscattered protons, a Mylar absorber (1.1 mg/cm^2) was placed in front of the detector.

In order to obtain the true nitrogen and boron distribution all the experimental data were deconvoluted with a deconvolution technique explained previously [8].

2.3. Rutherford backscattering spectroscopy

RBS was performed with a 2.4 MeV helium beam impinging on the surface of the specimen at normal incidence. The backscattered particles were collected at 175° from the incident beam direction. Light elements like nitrogen and oxygen are easily observable because we used thin aluminium foils. Therefore, there is no interference between Al and O signals. The RBS spectra were treated with the code SQUEAKIE written by Borgesen et al. [9]. The computer program calculates the depth profile of each element in the sample as a function of depth by solving a single set of linear equations for each element at each layer of the sample. Unfortunately, this code does not take into account the straggling effect of the helium beam in the sample.

3. Results

Fig. 1 shows the evolution of the RBS spectra for thin aluminium implanted with $5 \times 10^{17} N^+/cm^2$ during the anodic oxidation in the ammonium pentaborate solution. One can observe that the oxygen and aluminium signals appear at the surface and the height of those two signals corresponds to a stoichiometry close to Al_2O_3. The area of the oxygen signal is increasing with the applied voltage, whereas the nitrogen peak goes deeper and deeper. The RBS spectrum measured on the film oxidized at 200 V changes drastically from the others. There is a sudden increase of the oxide thickness and therefore it is difficult to obtain more information from this RBS spectrum because of interferences between N, O and Al signals. Nevertheless, by

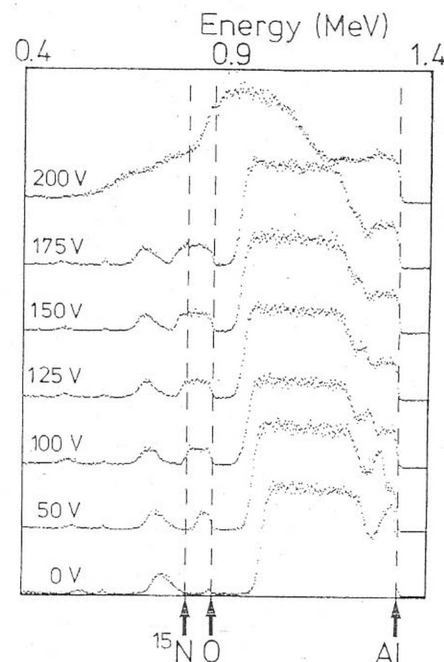

Fig. 1. Evolution of RBS spectra for thin aluminium films implanted with 5×10^{17} N^+/cm^2 and anodically oxidized at various voltages in an ammonium pentaborate solution.

rotating the foil over 180°, the O and N signals are well separated from the Al signal, and the contribution of the nitrogen can be easily subtracted from the O signal using the data obtained with NRA measurements.

The total atomic concentration of oxygen and aluminium in the oxide layer can be easily calculated from the RBS spectra. The evolution of the amount of oxygen atoms versus the applied voltage is shown in fig. 2a for pure aluminium and implanted aluminium with different doses [(1–10) × 10^{17} ions/cm^2]. For pure aluminium, the amount of oxygen increases linearly with the applied voltage. The film implanted at low dose (10^{17} ions/cm^2) shows the same behaviour as pure aluminium, but the oxide layer is growing more slowly. For the medium dose (5×10^{17} ions/cm^2) the oxide film grows linearly with the applied voltage, more slowly than the previous samples, but we observe a sudden increase of the oxygen concentrations between 175 and 200 V. The film implanted at the highest dose (10×10^{17} ions/cm^2), which is higher than the saturation dose (7.4×10^{17} ions/cm^2) [10], first shows a linear behaviour similar to the previous samples and then suddenly there is an increase of the amount of oxygen between 110 and 120 V.

From the boron depth profile, we can measure the total concentration of boron in the foil. In fig. 2b we have reported the evolution of the boron concentration versus the applied voltage. We can observe that the evolution of boron exactly follows the evolution of oxygen; for the samples implanted at higher doses there

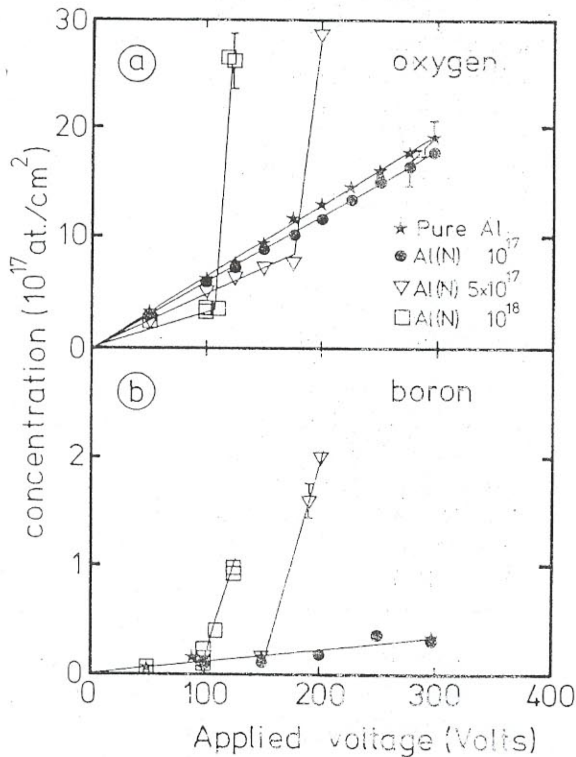

Fig. 2. Evolution as a function of the applied voltage during the anodic oxidation process of the total atomic concentration of (a) oxygen and (b) boron for pure and implanted aluminium.

is a sudden increase of the boron concentration when the oxide is growing rapidly.

We have also calculated the retained dose of nitrogen from the RBS spectra and from the depth distribu-

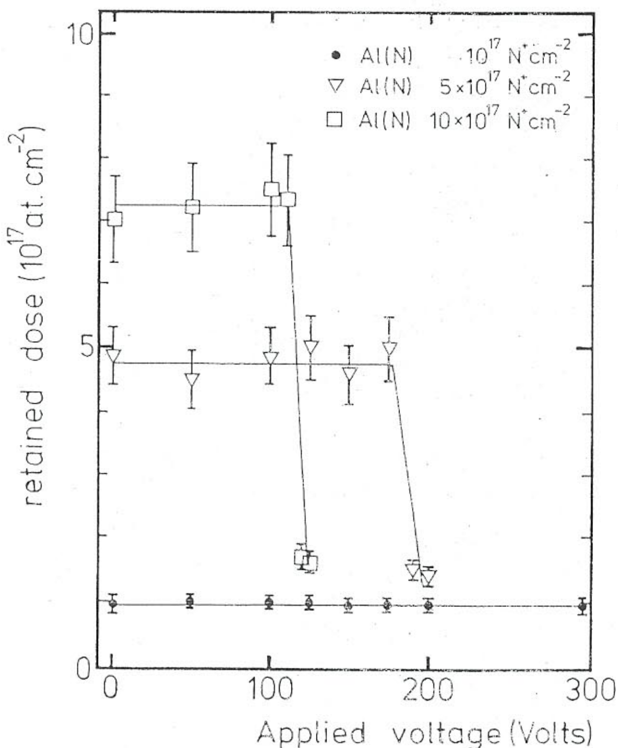

Fig. 3. Evolution as a function of the applied voltage during the anodic oxidation process of the nitrogen retained dose for aluminium implanted at different doses.

tion of nitrogen obtained by the NRA technique. NRA and RBS are both quantitative techniques and give the same results within 10%. The evolution of the retained dose versus the applied voltage is shown in fig. 3. For the lower dose, the retained dose stays constant (9.8×10^{16} at./cm^2), and for the medium and the higher doses of implantation, we observe the same behaviour: the retained dose of nitrogen is first constant, but a sudden decrease arises when the oxide layer is growing suddenly.

4. Discussion

A complete analysis of the RBS spectra indicates that the relative concentrations of aluminium and oxygen don't correspond exactly to the stoichiometry of Al_2O_3. This can be due to the presence of boron and probably hydrogen [11] in the oxide layer; in addition, since a RBS measurement gives only the areal density [at./cm^2], we are not able to discuss the evolution of the thickness of the oxide layer in more conventional units [nm]. Nevertheless, the thickness of the oxide layer is proportional to the total oxygen concentration and in the following discussion we will take the thickness in units of at./cm^2.

We can observe in fig. 2a that the growth of oxide is reduced for implanted specimens as well as the dose is increasing and aluminium nitride is present. This effect can result from the reduction of the amount of metallic aluminium atoms which are involved in the growth mechanism. It has been shown recently [10] that in the case of nitrogen implantation into aluminium, the width and the gradient of the nitrogen distribution are increasing with the dose because nitrogen diffused towards the surface. Thus, if the total amount of metallic aluminium between the oxide and the nitride layer is low (due to high-dose nitrogen implantation), the growth of the oxide is reduced compared to the non-implanted sample.

For the high-dose implanted samples, the sudden increase of the oxide layer is correlated to a sudden decrease of nitrogen (fig. 3). This has already been observed in ref. [1]. This experiment confirms that nitrogen escapes from the aluminium nitride through the oxide layer: bubbles have been observed in the electrolyte at the top of the sample (fig. 4). These bubbles are probably N_2 bubbles which result from the oxidation of the aluminium nitride. Nitrogen oxides are not expected here because of the low involved temperature. Moreover, the bubbles cannot be ammonia because the sample doesn't smell. After the escape of nitrogen, the depth profile of nitrogen is split into two components. These two components result from migration mechanisms which can be described as follows: film growth by anodic oxidation proceeds by Al^{3+}

egress and OH^- and/or O^{2-} ingress through a preexisting air-formed film (fig. 5a). These ionic fluxes lead to the formation of oxide layers at the metal/oxide interface and simultaneously at the oxide/solution interface (figs. 5b and c). Later this can be explained by Al^{3+} ions coming from the bulk through the oxide film (ejected into the electrolyte) and precipitating with the electrolyte anion species present under the influence of the field, while O^{2-} ions are able to go through the oxide and allow the growth at the metal/film interface by a solid-state mechanism [12–15]. When the anodic process has consumed all the metallic Al^{3+} ions available (staying between the oxide layer and the aluminium nitride layer), the growth of the film continues due to the electric field with the oxidation and the dissociation of the AlN compound because the heat formation of Al_2O_3 (−380 kcal/mole) is smaller than that of AlN (−80 kcal/mole). At that moment, free-atomic nitrogen is able to form molecular nitrogen and to migrate through the oxide layer which is more porous than the pure aluminium. This leads to the formation of N_2 bubbles in the solution at the surface of the sample (fig. 4). During the migration through the oxide, a certain amount of nitrogen precipitates; this gives a nitrogen distribution split into two components: the first one in the bulk due to nondissolved AlN and the second one near the surface due to a precipitation mechanism (fig. 5d). All nitrogen is in the oxide layer, and not only the first component as reported in a previous paper [1].

Fig. 5 has been established by overlapping the nitrogen distributions, because the aluminium nitrides are not modified at the beginning of the oxidation process. 40% of the oxide grows at the metal/oxide interface and 60% at the oxide/solution interface. Fig. 5d has been superposed to the others (5a–c) by assuming that the bulk component of nitrogen is due to nondissolved AlN. We can see that the proportion 40%–60% of the oxide growth is also conserved.

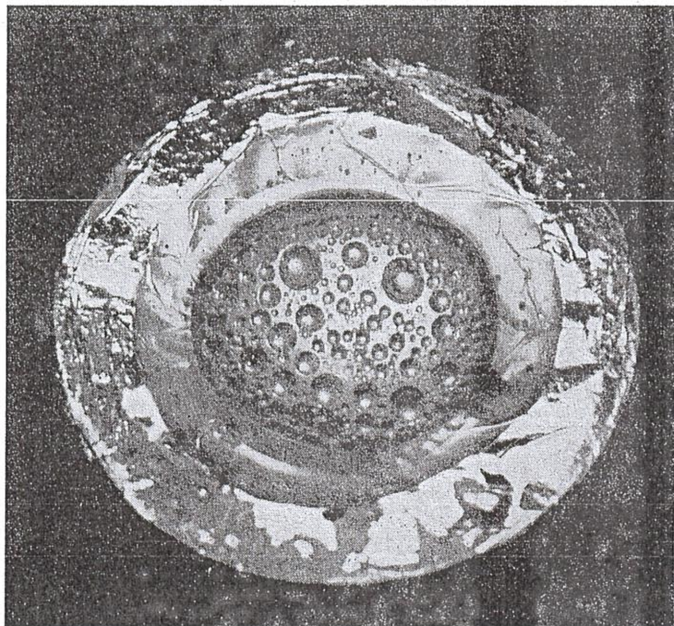

Fig. 4. Optical picture showing the nitrogen bubbles into the electrolyte after anodic oxidation at 200 V of a sample preimplanted with 5×10^{17} ions/cm^2.

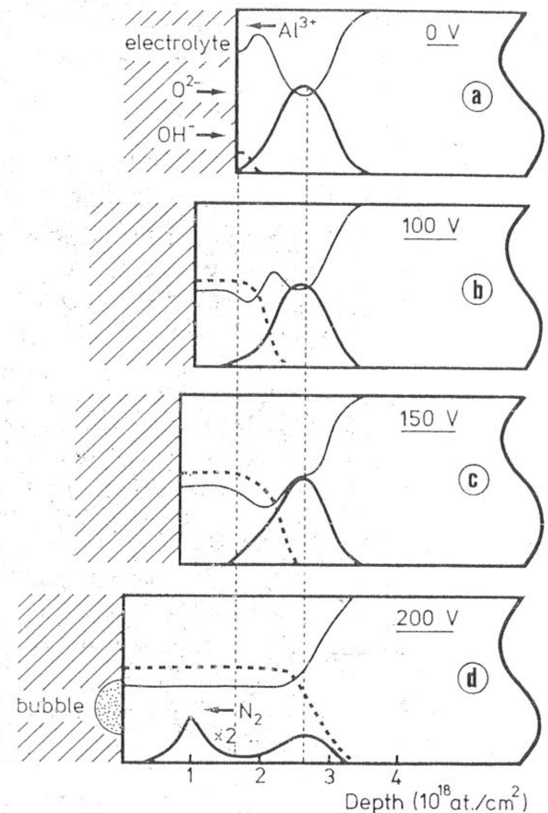

Fig. 5. Schematic presentation of the ionic migration mechanisms involved during the anodic oxidation of a sample preimplanted with nitrogen (5×10^{17} ions/cm^2) and oxidized at various voltages; the dashed line shows the oxygen depth profile, the thick full line the nitrogen depth profile and the thin full line the aluminium depth profile.

Another property observed during anodization of implanted aluminium is the change of color of the specimen. This property has been reported in a previous paper [1] and is not yet explained. The color of the implanted area depends on the fluence, the energy of implantation and the oxide thickness (and therefore the oxide composition). Another point not yet explained is the precipitation sites: why does nitrogen precipitate below the surface during the migration process?

Further experiments are planned in order to try to explain the optical properties of oxidized Al(N) and to characterize the structural and electronical properties of such a film.

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