

Atomic surrounding of Co implanted in AlN at high energy

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AlN bulk ceramic has been implanted with energetic Co ions. In order to accurately characterise the atomic surrounding of the implanted ions, X-ray absorption measurements were carried out at 80 K in the fluorescence mode at the Co K edge in the as-implanted and annealed states. Simulation of the EXAFS oscillations allowed us to identify a first stage where Co is inserted in the AlN matrix followed by a second stage where Co precipitates form.

Keywords : ion implantation, AlN, cobalt

1. Introduction

Ion implantation is often regarded as a tool to prepare out-of-thermodynamic equilibrium systems with improved surface properties. Since these properties depend on the phases formed during the slowing down process of the energetic incoming ion, it is important to characterise them from a crystallographic point of view and to look at their stability. We previously showed that Cu (Borowski *et al.*, 1994) and Ni ions (Traverse, 1997) implanted at room temperature with incident energies less than 100 keV in AlN form metallic clusters after an annealing treatment typically at 800°C for one hour under vacuum. From the analysis of the phases formed after implantation of different ions in different matrices, at about 100 keV, we deduced in a recent article that Co must precipitate to form clusters in AlN (Zanghi *et al.*, 2000). The goal of the work presented here is to identify the local environment of Co implanted at high energy (300 keV) in the AlN ceramic in the as-implanted state and after annealing at 800°C for 9 hours under vacuum. Because the incident energy is increased as compared to our previous work, the width of the implantation profile is larger. The consequence is that the ions are also located, on the average, at larger distances from each other than in the previous situation. Hence, the interaction with the matrix atoms and between themselves should be modified. Indeed, we found that Co ions are inserted in the AlN matrix in the as-implanted state, the thermal treatment leading to the formation of Co clusters with Co-Co bonds long of 2.50 Å as in bulk Co.

2. Experimental

Two pieces of AlN bulk ceramic were simultaneously implanted on the Aramis accelerator (Bernas *et al.*, 1992) with 5×10^{16} Co/cm² at 300 keV and room temperature. One sample was kept in the as-implanted state whereas the other one was annealed at 800°C for 9 hours under vacuum.

X-ray absorption spectroscopy was performed at the Co K edge on the H10 station of the DCI storage ring in Orsay (Gailhanou *et al.*, 2000). The samples were mounted in a liquid nitrogen cryostat and measured in the fluorescence mode, either with 0.5 eV steps on the 7600 – 7900 eV energy range (XANES) or with 2 eV steps on the 7600 – 8600 eV energy range (EXAFS). For comparison, a Co foil was also measured in the transmission mode. The absorption

coefficients were treated in the usual way, i.e. subtraction of the pre-edge, extraction of the oscillations and calculation of the Fourier transform on the 3 to 11 Å⁻¹ range (Michalowicz, 1991). Simulation of the filtered peaks was done using phase and amplitude either experimental or calculated depending on the type of neighbour.

3. Results

The XANES spectra obtained on the as-implanted and annealed samples are presented in Fig. 1.

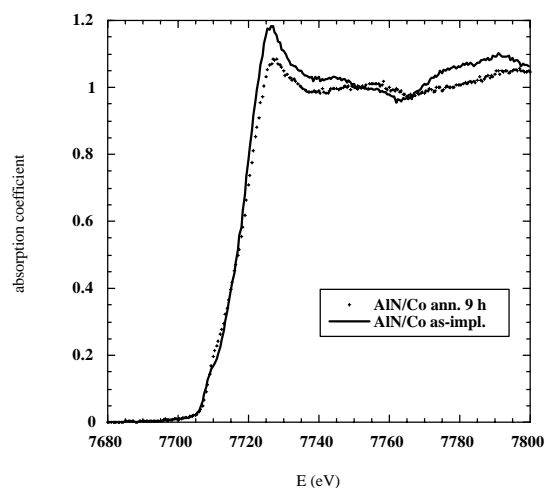


Figure 1 XANES at the Co K edge on the as-implanted and the annealed AlN implanted with Co at 300 keV.

An evolution between the two Co atomic surrounding due to the thermal treatment is already detected by the XANES modification, that is confirmed by the EXAFS oscillations and the Fourier transforms presented in Fig. 2 and Fig. 3.

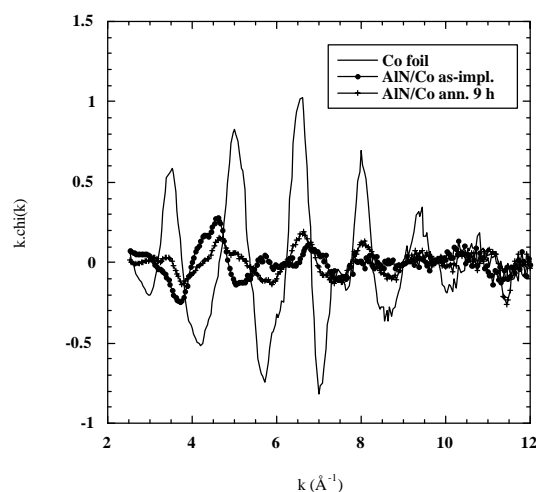


Figure 2 EXAFS oscillations at the Co K edge on a Co foil and on the as-implanted and the annealed AlN implanted with Co at 300 keV.

We note that the oscillations and the Fourier transforms are clearly different from those of a Co foil. A consequence is that, around Co, one must take into account other types of neighbours than Co only.

Moreover, it is clear from Fig. 3 that no long range crystalline order takes place even after the thermal treatment.

The two first peaks of the Fourier transform for the as-implanted sample and the first peak for the annealed one were filtered (from 1 Å to 3 Å uncorrected from phase shift) and the obtained oscillations fitted to obtain the type of neighbours, number and distances.

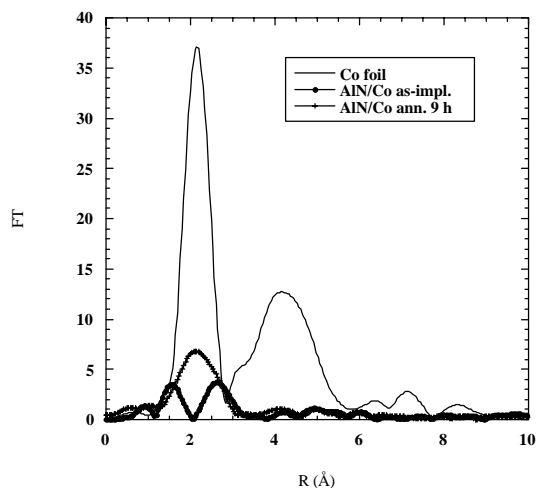


Figure 3 Fourier transforms on a Co foil and on the as-implanted and the annealed AlN implanted with Co at 300 keV.

Figs. 4 and 5 display the filters and their fits. Again, a strong evolution, over the whole k range, is noticeable between the as-implanted and annealed states, indicating an important modification of the Co atomic surrounding.

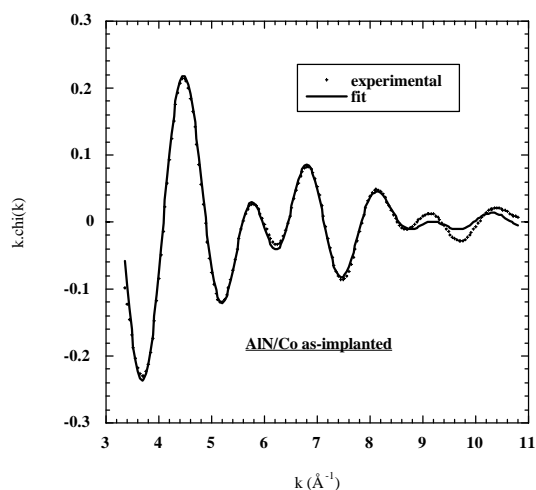


Figure 4 Filter of the two first peaks in the Fourier transform for AlN implanted with Co at 300 keV and its simulation.

During their slowing down process, Co ions loose their energy that induce a breaking of the Al-N and Al-Al bonds. There is thus a possibility for Co to bond to the matrix atoms. Since Al_xCo_{1-x} compounds have negative heat of formation (Miedema, 1988), a first attempt was to check the possibility of such compound formation. However, it was not possible to obtain fits of good quality, assuming

the existence of a first Al shell located at 2.47 Å as in Al_5Co_2 or at 2.50 Å as in $AlCo$, and a second Co shell located at 2.94 Å as in Al_5Co_2 or at 2.85 Å as in $AlCo$. By allowing the distances to vary, the fit gives an Al-Co shell located at about 2.23 Å, too short to be reliable.

Hence, we took another assumption, i.e. Co in substitution of Al in the AlN wurtzite structure. Due to the positive ionic character of this site, this is the only possible one for an incident Co ion. In this wurtzite structure, around an Al atom, there is a first shell of 4 N located at 1.89 Å, then 12 Al at 3.09 Å. The occupancy of the Al site by Co implies that Co is surrounded by a shell made of N atoms, although the Co-N bond is not thermodynamically favoured (Smithells, 1983).

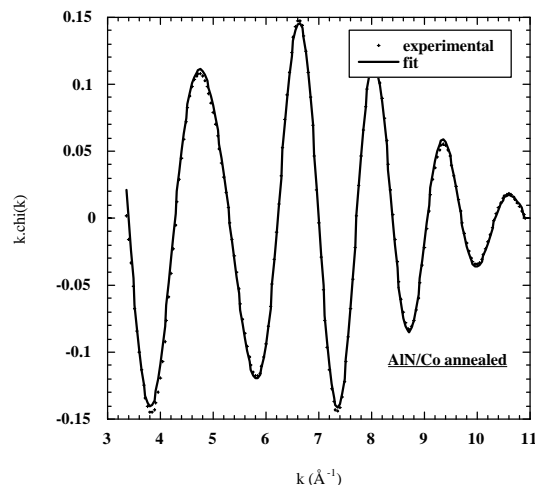


Figure 5 Filter of the first peak in the Fourier transform for AlN implanted with Co at 300 keV then annealed and its simulation.

For the N shell, we took the phase and amplitude calculated by McKale (McKale, 1988). For the Al shell, as Si is the Al neighbour in the periodic table, we took the phase and amplitude extracted from the first filtered peak of a $CoSi_2$ compound measured at the Co K edge. For Co-Co, we took the phase and amplitude extracted from the Co foil. Results of the fitting procedure are presented in Table 1.

Table 1 Results of simulation as compared to Al environment in AlN

Type of neighbour	AlN/Co as-implanted	AlN/Co annealed	Al in AlN
N	4 at 2.03 Å $\sigma = 0.098$ Å	2 at 2.03 Å $\sigma = 0.090$ Å	4 at 1.89 Å
Al	8 at 3.03 Å $\sigma = 0.088$ Å	6 at 3.02 Å $\sigma = 0.080$ Å	12 at 3.09 Å
Co	4 at 3.28 Å $\sigma = 0.154$ Å	3 at 2.50 Å $\sigma = 0.045$ Å	

In the AlN/Co as-implanted sample, around Co, the first N shell with 4 atoms is identified. Then the second shell of 8 Al atoms is found located at 3.03 Å, followed by 4 Co at 3.28 Å. This result supports the assumption of Co in substitution of Al in the AlN matrix.

After annealing, the Co-N and Co-Al distances are kept, but the number of N and Al neighbours has decreased to half the value in AlN. The noticeable evolution is that the Co shell has disappeared and a new one is created where the Co atoms are now located at a

distance of 2.50 Å, i.e. the distance in bulk Co. This large distance reduction, out of uncertainty, is a strong indication of Co precipitation to form clusters.

The Debye-Waller factor is systematically slightly decreased by the thermal treatment as expected. It is rather small in the case of the Co clusters (0.045 Å) in agreement with previous results for Ni in AlN (Zanghi *et al.*, 2000).

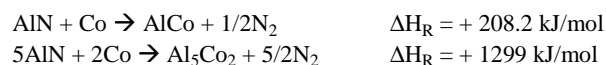
4. Discussion

Due to the large number of parameters used in the fitting procedure, we must consider that the uncertainty on N is not better than ± 1 and ± 0.02 Å on R . Thus, in the following, we will discuss the motion of the Co atoms from the Al site in AlN to Co cluster, rather than the absolute parameters values.

Although unexpected in view of the positive heat of formation of the Co_3N nitride (Smithells, 1983), the assumption of Co substitution to Al in the AlN matrix appears reasonable as indicated by the surrounding that is deduced from the fit. There are 4 N at a larger distance than in AlN, this can be due to the Co ionic radius (0.65 Å for Co^{3+}) larger than the one of Al (0.57 Å for Al^{3+}) (Smithells, 1983). An Al shell is present at a distance a little bit shorter than in AlN with only 8 atoms. However a Co shell is detected, the total amount of Al+Co atoms being 12, i.e. the expected number of Al atoms in AlN. One can thus consider that part of the Al shell is filled with Co atoms.

This situation appears to be strongly unstable under thermal treatment in the conditions used here. Part of the Co atoms went out of the Al site, as indicated by the fact that only 2 N, half of the initial value, and 6 Al are then measured and also that the Co shell located at 3.28 Å disappeared. The Co ions that have left the Al site precipitate to form Co clusters as indicated by the Co-Co shell located at 2.50 Å.

This result is in full agreement with those previously published on Cu (Borowski *et al.*, 1994) and Ni ions (Traverse, 1997) implanted in AlN. The interpretation, presented in Zanghi *et al.* (2000) is that the final system can be predicted by writing the reaction equation, i.e.



The positive heat of reaction indicates that the AlCo and Al_5Co_2 compounds cannot form in agreement with the impossibility to get good fits with these assumptions. The possibility of Co_3N formation is not considered as its heat of formation is positive (Smithells, 1983). Thus the only remaining possibility for Co is to form clusters.

The Al substitution by a Co ion that is observed here in the as-implanted state is not in contradiction with what is written above. It represents the first stage of a process where the stopping site for Co after the implantation process is the Al site. This site being unstable as explained by the positive heat of formation of Co_3N (Smithells, 1983), thermal energy induces a migration out of this site and a Co precipitation. The annealing conditions used here are not sufficient to induce a total Co precipitation. The temperature should be probably higher than 800°C.

Note that a substitution of Al by Ti was already observed just after Ti implantation in AlN (Borowski *et al.*, 1994). However, since the Ti-N bond is thermodynamically favoured, this substitution is not unexpected. Indeed, the TiN compound is finally formed at the expense of AlN after annealing.

The fact that part of the Co ions have precipitated and that part of them are still in the Al sites is not contradictory with the Ni and Cu precipitation mentioned above. These ions were implanted at lower energy, thus are located closer from each other than in the case described here. Taking into account the measured width of the implanted profiles and assuming that the ions are distributed over this width on a cubic lattice, a crude evaluation of the average distance between Co ions after implantation is 4.2 Å for 80 keV incident energy and 6.3 Å for 300 keV incident energy. These distances are clearly larger than those measured by XAS, i.e. 2.5 Å for 80 keV where clusters have already formed and 3.28 Å for 300 keV (Table 1). This can be interpreted by saying that the implanted ions have already started to interact during the implantation process. As the interaction length is probably finite, supplementary energy is required in the latter case to induce cluster formation than in the former one.

5. Conclusion

Co ions implanted at 300 keV and room temperature were found to occupy the Al site in the AlN matrix. In this site, Co is surrounded by a N shell, in contradiction with the fact that the Co-N bond is not thermodynamically favoured as indicated by the positive heat of formation of Co_3N (Smithells, 1983). However this site is unstable and the thermal treatment leads to Co mobility out of this site to the benefit of Co cluster formation. Indeed this latter system is the one predicted when one writes the reaction equation between AlN and Co. The as-implanted state appears thus as an out of equilibrium system, unstable under annealing.

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