RADIATION DAMAGE EFFECTS IN NB+ IMPLANTED SAPPHIRE AFTER ANNEALING

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ABSTRACT

Niobium ions of 380 keV energy have been implanted at 300k in sapphire with a dose of 5×10^{16} ions/cm^2 and subsequently thermal annealed up to 1100 $^{\circ}$C at reducing atmosphere. The behavior of the radiation damage produced by ion implantation followed by annealing is investigated using optical absorption technique and X-ray photoelectron spectroscopy (XPS). It is found that different defects annealed are dependent on the annealing temperature owing to different mechanisms which are proposed on the basis of the optical absorption measurement, and the implanted niobium in sapphire is in different local environments with different charge states after annealing, which are analyzed by XPS measurements.

1. INTRODUCTION

Ion implantation is a convenient method by which to introduce impurities into ceramic at a definite depth and definite atomic concentration in order to produce a new material layer with novel mechanical, optical, chemical and electrical properties. On the other hand, the charge state of the implanted ions can be associated with the lattice defects created near the end of ion range, since the implanted ions can interact with the lattice defects. The interaction of energetic ions with ceramics is different from that with metals in several significant ways. Ceramics generally contain two or more chemical species that are distributed over different sublattice. Usually in an ordered fashion. The energy to displace each species from its lattice and the energy for chemical bonds with incident ions are always different.   However, until recently, there were only a few investigations on chemical effects of ion implantation in ceramics[1-3].

For a better understanding how the implanted ions interact with the host material. We give information on the behavior of the defects induced by Nb+ implantation and the chemical states of the niobium in sapphire after annealing at a reducing atmosphere by using optical absorption measurements and X-ray

photoelectron spectroscopy (XPS) analysis.

2. EXPERIMENTAL

($01\bar{1}2$) sapphire platelets of 12×8×0.3 mm^3 with an optical grade as substrates were annealed at 1450°C in air for 12h before ion implantation in order to eliminate strains. Niobium ion implantation was performed at room temperature at Takasaki, JAERI. Ion energy, current density and dose were 380 keV, 1-1.5×10^{-6}A/cm^2 and 5×10^{16} ions/cm^2, respectively. The implanted samples were annealed under flowing Ar+3%H$_2$ gas in steps of 100°C from 500 to 1100°C. A schematic graph of such an annealing procedure is shown in Fig.1. Optical absorption measurements using an O-3210 micro-spectrophotometer were taken between 85 and 910 nm. The XPS measurements were carried out with a surface analyzer (VG scientific Ltd.) employing Mg (1253.6 eV) as the exciting radiation. A 4keV Ar$^+$ ion beam was used to etch the sample to get the depth profile.

3. RESULTS AND DISCUSSION

For oxide materials, elastic collisions are by far the dominant processes for producing vacancy-interstitial pairs[4]. In sapphire, the requirements of overall electrical neutrality may give rise to charged point defects and to impurity-defect complexes that can be detected and identified by spectroscopic means. The annealing behavior of the retained point defects in Nb$^+$ implanted sapphire can be estimated on the basis of the variation of the measured optical densities (ODs) of F-type centers. The number of color centers produced per incident ion N was determined from Smakula's equation in the form

$$N = 2.00 \times 10^{17} \frac{n}{f_{ij}\varphi(n^2+2)^2}(ODW_{1/2}) \tag{1}$$

where f_{ij} is the oscillator strength for the transition[5], φ is the ion dose in cm^{-2}, n is the refractive index at the band peak[6], OD is the peak optical density of the different spectrum, and $W_{1/2}$ is the FWHM of the band, in eV. The prominent absorption band centered at 204 nm (near 6.1 eV) has been assigned to F centers with two electrons trapped at an anion vacancy[7], at 4.8 eV(230 nm), 5.4 eV(260 nm) and 6.3 eV to F$^+$ center (an oxygen vacancy with one trapped electron) responsible for three transitions[5], and at 4.13 eV(300 nm) to F$_2$ center(two-to-four electrons trapped at a next-nearest-neighbour anion vacancy pair)[8]. These bands are obtained by Gaussian fitting the experimental spectrum
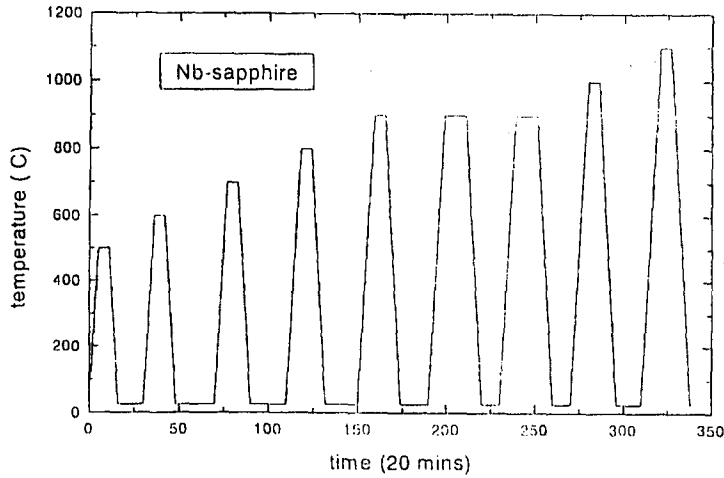
within the section of 200 to 340 nm shown in Fig.2.

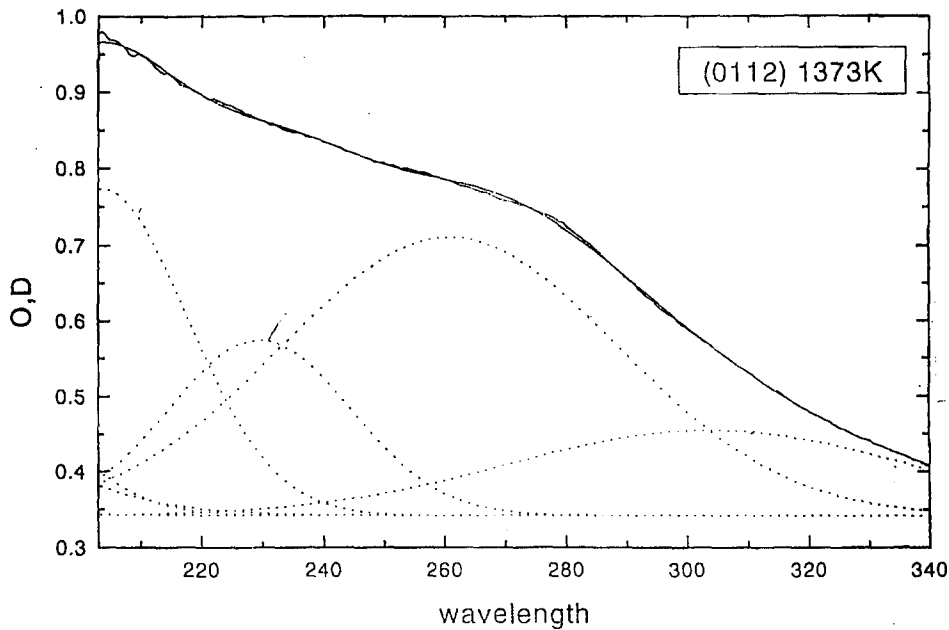Fig.1. A schematic diagram of annealing procedure.

Fig.2. Optical absorption of Nb^+ implanted sapphire dissolved into bands by Gaussian fitting.

Fig.3 shows the absorption curves of the samples after annealing. It can be seen that the optical densities for the sample decreased strongly after annealing at 1100℃ with a series of steps. But it is noted that defects still exist such as isolated F-type centers. Summarily on the basis of mechanisms in radiation damage annealing out, three stages with annealing temperature can be distinguished. In the first stage with annealing temperature from 500 to 900℃,
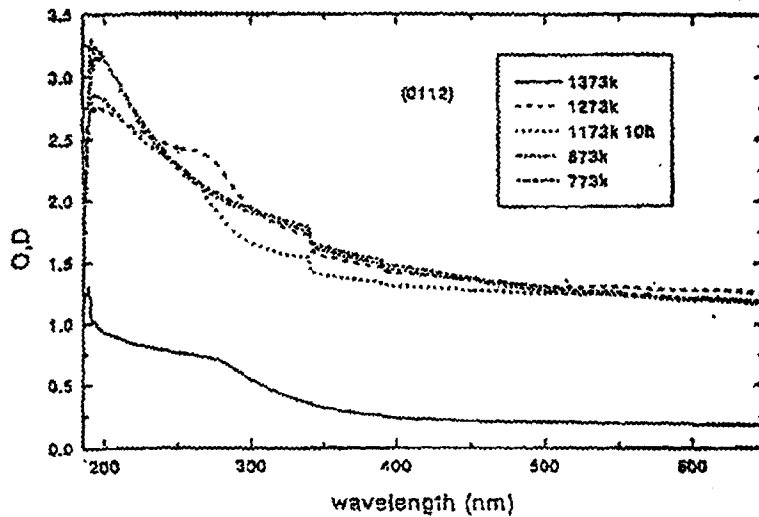
Fig.3. Optical absorption of (01Ī2) samples with different steps of annealing temperature for 2h at each step except at 1173k for 10h.
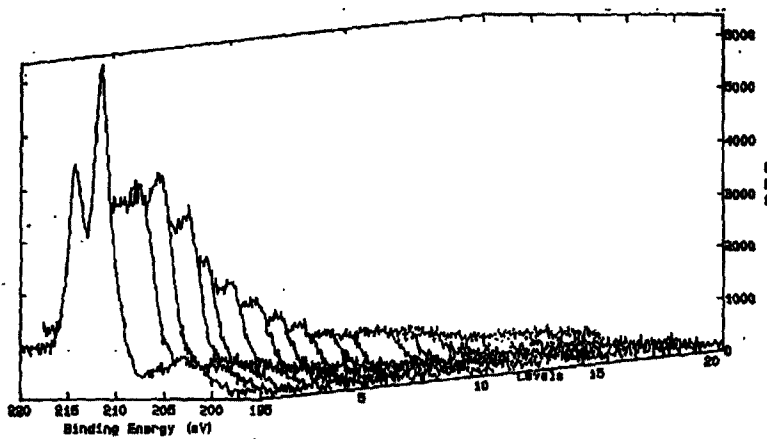

Fig.4. Depth profile for Nb implanted into sapphire after annealing at 1100℃.

thermally unstable, closely spaced anion Frenkle pairs surviving the displacement events are combined, subsequent break-up of the clusters of anion interstitial takes place. In the second stage from 900 to 1000℃, diffusion and dissociation of impurity-oxygen vacancy complexes lead to formation and growth of the implanted niobium precipitates and voids attached. In the third stage above 1000 decrease in concentration of F-type centers. More detail can be seen in the paper[9]. Here it should be emphasized that there is a bump near 286 nm after annealing at 1100℃ shown in Fig.3. Discussion about it will be made in the following section.

Now let us focus on the chemical states of the implanted niobium after annealing. Fig.4 shows the Nb3d spectra at the different positions from the surface to deeper range in the sample after annealing at 1100℃ via a series of

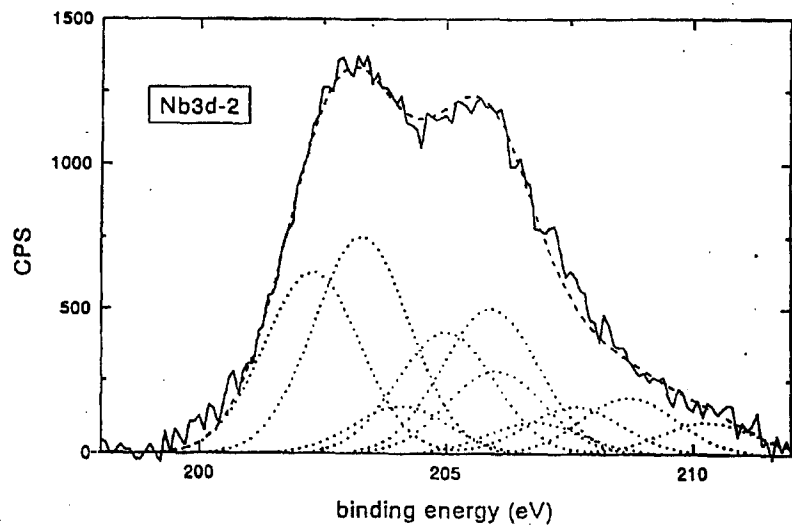defects including stable defects are annealed out leading to a dramatical

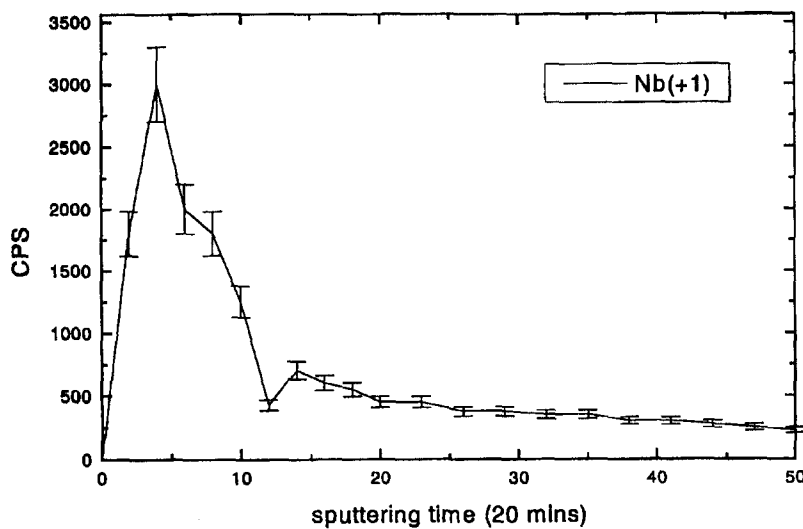Fig.5. The niobium XPS spectra for the annealed sample Nb3d-2: after ion etching for 80 mins.

Fig.6. Depth profile of the NB^{+1} charge state of niobium for the annealed sample.

steps from 500°C to 1100°C in the Ar+3%H_2 atmosphere. The results show that most of the resident niobium moved towards the surface due to that the epitaxial recrystallization of the region damaged by ion implantation causes the migration of the implanted atoms towards the surface where the implanted species have low or no solid solubility in the substrate matrix at the temperature range concerned. Another phenomenon is that the niobium depth profile exhibits a rather long tail extending to more deeper region after annealing. This means that some niobium species migrated to the opposite direction. Obviously, such a behavior must be linked with some defects retained in the sample.

In order to make clear which species was playing this behavior, a deconvolution was chosen for the Nb3d spectra by using Gaussian fitting shown in Fig. 5 as an example. Apart from the components of Nb^{+5}, Nb^{+4} Nb^{+2} and Nb^{0} which are consistent with those given by published papers[10,11], a new charge state of niobium labeled Nb^{+1} should exist to well fit these experimental Nb3d spectra. The results show that niobium in sapphire after annealing is in different local environments with different charge states. Nb^{+5} and Nb^{+4} were mostly distributed on the top surface and decreased rapidly with depth, these states are caused by the incorporation of foreign oxygen. The metal niobium Nb^{0} state is due to the annealing in the reducing atmosphere and most of niobium atoms moved to the area just below the top surface to form metallic precipitates. Nb^{+1} state is distributed over a wide range shown in Fig.6. The charge state of Nb^{+2} is also distributed over a wide range[12]. It should be pointed out that Nb^{+1} state entered to a deeper area in sapphire after annealing. According to the optical absorption measurements, defects such as F-type centers decreased rapidly after annealing but existed still. So it is reasonable to consider that these states seem to be associated with defects to form impurity-defect complexes retained in the sample.

4. CONCLUSIONS

Niobium implanted into $(01\bar{1}2)$ sapphire after annealing with a series of steps from 500 to 1100 °C in a reducing atmosphere was investigated by absorption measurement and XPS analysis. The following conclusions may be drawn from the results presented in this paper.

1. After annealing at 1100°C, the O.D value decreases dramatically, this means the defects retained in the sample which are indicated by F-type centers are almost annealed out, but not completely.

2. Niobium in sapphire is in different local environment with different charge state after annealing.

3. Low charge state Nb^{+1} as well as Nb^{+2} are distributed over a wide range to a deeper area in sapphire after annealing. It seems these states are responsible for the niobium atoms which are associated with defects retained in sapphire.

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