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# Formation of Nitride $Cu_3N$ by MeV N-Ion Implantation into Cu*

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*Experimental evidences are presented to show the formation of nitride, $Cu_3N$, in pure Cu sample by N-ion implantation. This result is obtained in the case of MeV ion implantation. Previous experiments showed that this compound can not be formed by N-ion implantation into Cu at incident energy of about 100 keV. This finding indicates there exist certain differences in phase formation by ion implantation at the two energies.*

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In recent years, high-energy ion implantation has been an attractive subject. One important aspect is the anomalous enhancement in defect production in some metals irradiated by high-energy ions, in which high electronic stopping power is responsible.[1] Besides the fundamental interest, there is also a search for practical applications such as in metal modifications and buried insulator-layer formation in semiconductors. In the past, the incident energy in N implantation of metals is around 100 keV, mainly due to the limitation in ion-implantor. Recently, MeV ion-implantors with high beam-currents are available. For example, the implantor has been used to search the effects of MeV N-ion implantation in Ti and Fe.[2,3] It has been found[2,3] that there exist different aspects for structure modifications and properties of 1MeV and 100 keV implanted metals.

To our knowledge, copper nitride, $Cu_3N$, has never been formed artificially by direct reaction of nitrogen and copper. Up to 1670 K, nitrogen is insoluble in both solid and liquid copper.[4] It was also reported that N-ion implantation at an energy of about 100 keV can not form Cu nitride $Cu_3N$ (Refs. 5, 6) and the saturation concentration probably limited by sputtering, is only 18 at.% N.[7] According to sputtering theory,[8] sputtering yields of Cu bombarded by N-ion at 1.0 MeV and 100 keV are 0.3 and 1.1, respectively (see Table 1). From theoretical consideration on saturation concentration limited by sputtering, the obtained peak value of N concentration in 1.0 MeV implantation should be larger than 25 at.% N. Such a concentration means that formation of the nitride $Cu_3N$ should be possible, if chemical stoichiometry is the determinating factor in the nitride formation.

Samples of pure Cu (99.99%) of 3 mm thickness were mechanically polished to optically flat finish. N-ion implantation was carried out using the implantor mentioned

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above. Areas of 9-mm diam were irradiated at a chamber pressure of $10^{-4}$ Pa for a series of doses in the range $1.0 \sim 2.2 \times 10^{18}\, N^+/cm^2$. During implantation, the temperature of the samples was monitored as less than 510 K by a Pt-resistance attached on the back side of samples. The beam current was about $20\,\mu A/cm^2$.

After implantation, the surface of samples remained smooth and shiny. X-ray diffraction (XRD) analysis was performed. Figure 1 shows a XRD spectrum from the sample implanted with dose of $2.2 \times 10^{18}\, N^+/cm^2$, where Cu K$\alpha$ radiation was used. Clearly the diffraction peaks of $Cu_3N$ from crystalline planes of (111), (200), (220) and (310) are observed. Table 2 compares the observed four diffraction peaks from the new phase formed in the sample with the standard values of the $Cu_3N$ card.[9] We have also checked that these peaks can not be attributed to any Cu oxide or carbide. This shows that cubic $Cu_3N$ ($ReO_3$ structure type) has indeed been formed in the implanted sample.

For high dose implantation, N concentration profile could be analyzed by Rutherford backscattering spectrometry (RBS) by observing the decrease in matrix signal due to dilution. Figure 2 is an example of a 2.0 MeV $^4He^+$ RBS spectrum taken from a pure Cu sample before and after N-ion implantation. This result has been comfirmed by reproducibility of tests. From the ratio of the RBS yields of implanted and unimplanted Cu, the N concentration distribution can be evaluated by a method described in Ref. 2. It is interesting to remark that the peak value of N concentration in this sample is not more than 25 at.% N as expected from theory, but only about 20 at.% N, as revealed by RBS. In fact, RBS analysis shows that the peak value of N concentration remains almost the same after implantation for dose higher than $1.7 \times 10^{18}\, N^+/cm^2$. It is also seen from the RBS spectrum that diffusion of nitrogen from the implanted Gaussian profile has occured. Comparing nitrogen implanted in Ti and Fe,[2,3] the diffusion coefficient of N in Cu must be significantly larger than in Ti and Fe. It is assumed from both results of RBS and XRD that $Cu_3N$ is not a buried layer but rather the tiny grains immersed in bulk Cu.

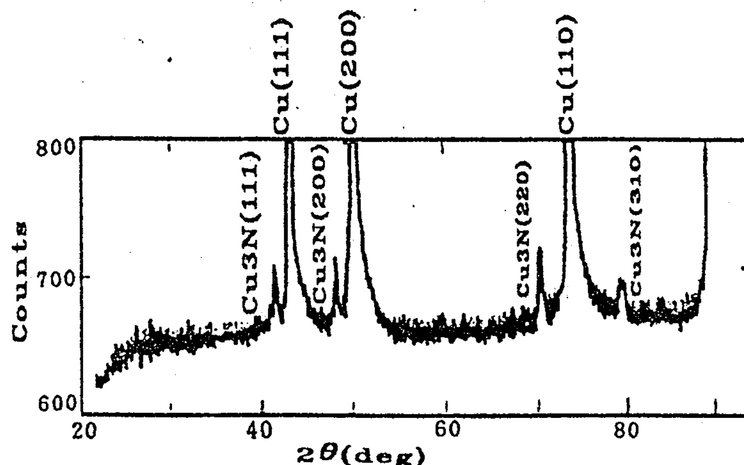


Fig. 1: XRD spectrum for Cu specimen implanted with $2.2 \times 10^{18}\, N^+/cm^2$ at 1.0 MeV.

In discussing the mechanism of metal nitride formation by ion implantation, the heat of formation of metal nitride and structural correlations between the nitride and bulk metal phases were in general considered. In the case of copper, the heat of formation of $Cu_3N$ is +4 kJ/mole (520 K)(Ref. 10) and $R_v$ which is defined as the molar volume

expansion ratio of a nitride to a matrix metal, is 1.56. In Ref. 6, $R_v \leq 1.3$ was suggested as a necessary condition for nitride formation. Such data indicate that a higher activation energy is needed for $Cu_3N$ formation from the viewpoint of thermodynamic condition and readiness of structure transformation. Such considerations however are the same for implantations with MeV and 100 keV.

Table 1: Comparison of parameters of ion implantation at 1 MeV and at 0.1 MeV in the N-Cu system. Sputtering yields were estimated from Sigmund theory,[8] other data in the table were given by TRIM[11] calculation.

| Ion energy (MeV) | 0.1 | 1 |
|---|---|---|
| Range (nm) | 113 ± 48 | 776 ± 138 |
| Sputtering yield (atoms/ion) | 1.1 | 0.3 |
| Electronic energy loss fraction (%) | 57.8 | 89.0 |
| Peak value of electronic energy loss (eV/nm) | 500 | 1650 |

Understanding why it is possible to form $Cu_3N$ by MeV implantation, while at the low-energy this is not possible, may be brought to light if we consider the differences of the kinetic process, e. g. nuclear and electronic energy loss differences between two implantations (see Table 1). Results by TRIM simulations[11] gave that 89.0% of the incident energy of 1.0 MeV implantation is electronic energy loss, while for 100keV implantation this is only 57.8%. Furthermore, the peak value of electronic energy loss in MeV implantation is three times more than that in low energy implantation. On the other hand, it is estimated by a method in Ref. 12 that there is no much difference in energy densities for atomic collision cascades, caused by primary knock-on atom of Cu for MeV and for 100 keV N-ion implantation, due to the formation of subcascade. Therefore, a higher activation energy determined by electronic stopping power in the case of MeV implantation should be important for $Cu_3N$ formation. If locally the N concentration in the Cu matrix approaches, by fluctuations, the chemical stoichiometry of $Cu_3N$ after implantation at a high enough

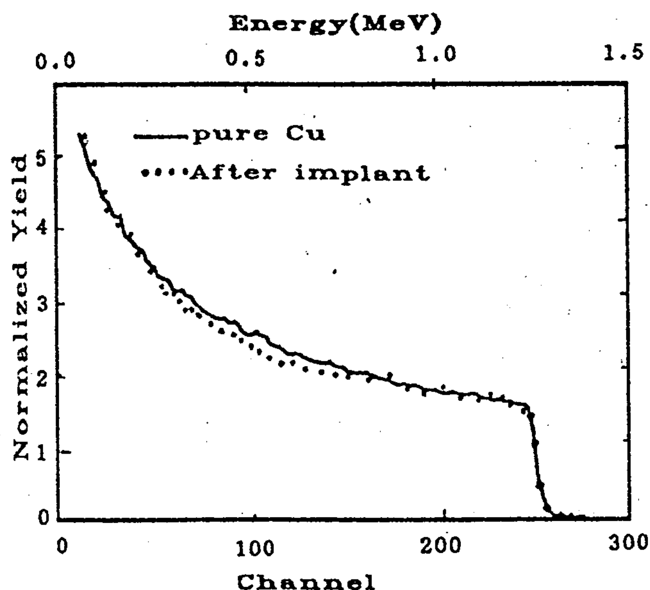


Fig. 2 : RBS spectra from the virgin Cu sample and MeV implanted Cu sample. The difference between the two spectra indicates N profile.

dose, and if additionally an electronic energy spike with high-energy density overlaps this location, formation of $Cu_3N$ there would be possible.

Table 2: Phase identification for Cu implanted at 1 MeV to a dose of $2.2 \times 10^{18}$ $N^+/cm^2$. m: medium, s: strong, w: weak.

| Peak | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $2\theta$ | 41.41 | 48.15 | 70.55 | 79.80 |
| *d* (observed) | 2.18 | 1.89 | 1.33 | 1.20 |
| Intensity (observed) | m | m | s | w |
| *d* (standard) | 2.20 | 1.90 | 1.35 | 1.20 |
| *hkl* (plane) | 111 | 200 | 220 | 310 |

In summary, nitride $Cu_3N$ has been formed directly by MeV N-ion implantation into Cu. It appears that MeV implantation is more powerful than low-energy implantation in the formation of nitride. The high electronic excitations followed high-energy N beam slow-down is responsible for the observed effect.

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