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Range distribution of low-energy nitrogen ions in metals

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The range distributions of N_2^+ in copper and silver have been determined for energies up to 5 keV. The distributions show a sharp peak at the surface along with a deeper shoulder or secondary peak and a long tail into the sample, contrary to theory which predicts only a near-Gaussian distribution in the sample. Careful examination indicates that neither the possible physical or chemical properties alteration by ion bombardment nor experimental error is the cause of the enrichment of nitrogen near the surface and therefore confirms the presence of this peak as part of the distributions. The energy dependence and the depth of the secondary peak, however, are in reasonable agreement with those predicted by available theories for the projected range distribution of implanted species.

INTRODUCTION

When an energetic ion impinges on the surface of a solid, it exchanges energy with the stationary atoms of the target. These transfers of energy could change the physical and chemical properties of the surface and the bulk material. A theoretical analysis for ion-implantation ranges and distributions into materials was reported by Lindhard, Scharff, and Schiøtt,[1] widely called the LSS theory. It has been the source of most implantation range calculations.[2] Calculated values of R_p for various incoming particles (Z_1,A_1) and stopping substances (Z_2,A_2) have been reported by Winterbon[3] and Littmark and Ziegler.[4] Also, simple formulas for range and projected range calculations corresponding to various values of incident ion energies based on the formalism of LSS theory are given by Schiøtt[5] and Sigmund.[6] LSS theory has been shown to be applicable above 10 keV.[7] We wish to determine the interaction of low-energy (500 eV to 5 keV) light ions with surfaces and as a result require information on the applicability of LSS theory and its modifications[5,7] to projected ranges in this low-energy ion regime. The present work, therefore, is a study of the depth distributions of low-energy nitrogen ions (1–5 keV) in polycrystalline copper and silver samples. Projected ranges and energy dependence of ranges are determined from experiment and compared to the calculated values using the analysis by Sigmund and Schiøtt.

EXPERIMENTAL PROCEDURE

High-purity (99.95%) copper and silver samples were prepared and polished smooth with 0.05-μm polishing paste. The samples were then cleaned and mounted on a portable carousel in a UHV chamber for ion bombardment and depth profiling. The samples were cooled to liquid-nitrogen temperature and kept at this temperature during the experiment to minimize the possible normal diffusion of ions inside the host material. The base pressure in the chamber was 1×10^{-9} Torr and was set from 1×10^{-6} to 1×10^{-7} Torr of nitrogen during nitrogen-ion bombardment depending on the energy of the ions. The samples were bombarded at normal incidence with an ion gun of the type reported by Schubert and Tracy.[8] The experiment was done for different ion energies ranging from 1 to 5 keV in 1-keV intervals and for fluences ranging from 2×10^{14} to 5×10^{16} ions/cm^2.

Following nitrogen bombardment, analysis was performed by means of Auger electron spectroscopy (AES) to determine the depth distribution of nitrogen ions inside the copper and silver samples. Using the inert-gas ion-bombardment stripping technique, a calibrated thickness of the material was removed by bombarding the surface with the probing ion beam and the amount of nitrogen remaining in the sample was determined from the nitrogen AES peak-to-peak height. To achieve maximum depth resolution, the ion beam during depth profiling and the electron beam during AES analysis were held at glancing angles to the surface (75° and 60°, respectively, to the surface normal). The probe ion used in depth profiling was 1-keV argon with a beam current of about 30 μA and a beam area of about 3 cm^2. During sputtering, the argon pressure was controlled to a constant value of 6×10^{-5} Torr. The sputtering rate for copper and silver was determined by means of a quartz-crystal thickness monitor. A given mass of copper or silver was first evaporated onto the calibrated quartz crystal. The coated quartz crystal was then positioned in place of the implanted sample and argon ion bombarded under conditions equivalent to those operable in depth profiling. The rate of mass removal was then determined from the change in frequency of the quartz-crystal oscillator and related to thickness removed by assuming uniform removal of material. The sputtering rate is expected to be different for pure elements and multicomponent materials. However, in the present case the nitrogen concentration is low (less than 6% at the surface decreasing to a fraction of a percent in the bulk) and the sputtering rate as determined from the expression used by Sigmund[9] is to within 5% equal to that of pure copper and silver. Under the noted argon sputtering beam conditions, the rate of removal was determined to be 12 ± 1 and 19 ± 1 Å/min for copper and silver, respectively.

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RESULTS

Figure 1 shows the measured range distributions of 4-keV nitrogen ions in copper and silver as defined by the peak-to-peak intensity of the nitrogen Auger peak (389 eV) versus the thickness of material removed. The nitrogen concentration at the surface was determined from the nitrogen peak-to-peak values in the Auger spectra using published sensitivity factors for nitrogen, copper, and silver (Fig. 2). Adsorption of nitrogen on the surface of the metal samples from the 1×10^{-6} to 1×10^{-7} Torr background N_2 pressure was checked for and observed to be nonexistent at 80 K (within the 0.2% monolayer resolution limit of the spectrometer) for silver and present at the value of $\sim$1.2% monolayer at 80 K for copper after exposure to 1 h of N_2 at 1×10^{-6} Torr. Any recoil implantation resulting from the very small amount of surface-adsorbed N_2 on copper would not significantly affect the measured nitrogen distributions. The range distributions in Fig. 1 indicate a sharp peak (or localization of nitrogen atoms) near the surface of the sample (within the first approximately 10 Å) along with a deeper lying secondary peak and a long tail into the sample. The shoulder or secondary peak of the experimental distributions conforms well to the most probable projected range predicted by theory.

Figures 3 and 4 show the energy dependence of the distribution for N_2^+ on silver and copper, respectively. Although there is a relative decrease in the surface peak at high energies, it is present in all distributions in this range of energies. The broadening of the distributions with increasing energy is clear from the figures, confirming the theoretical predictions.[6,10,11] The secondary peak max-

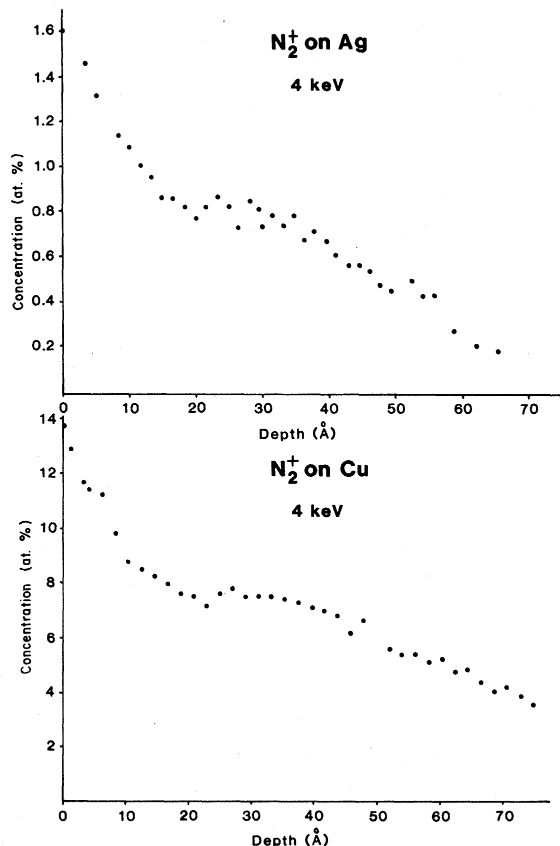

FIG. 1. Range distributions of 4-keV nitrogen ions in copper and silver. The ordinate represents the nitrogen concentration which is determined from the peak-to-peak intensity of the nitrogen AES peak (389 eV) as compared to the substrate AES signal.

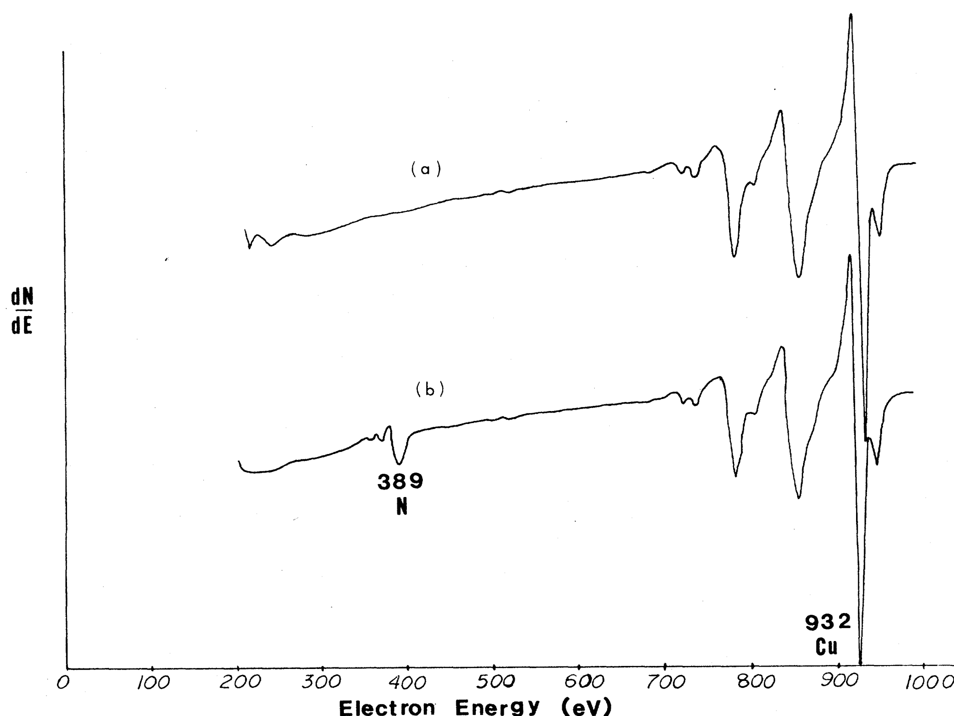

FIG. 2. (a) Auger spectrum of a clean copper surface; (b) Auger spectrum from the surface of the copper bombarded with 3-keV nitrogen ions at a fluence of about 5×10^{15} ions/cm^2.

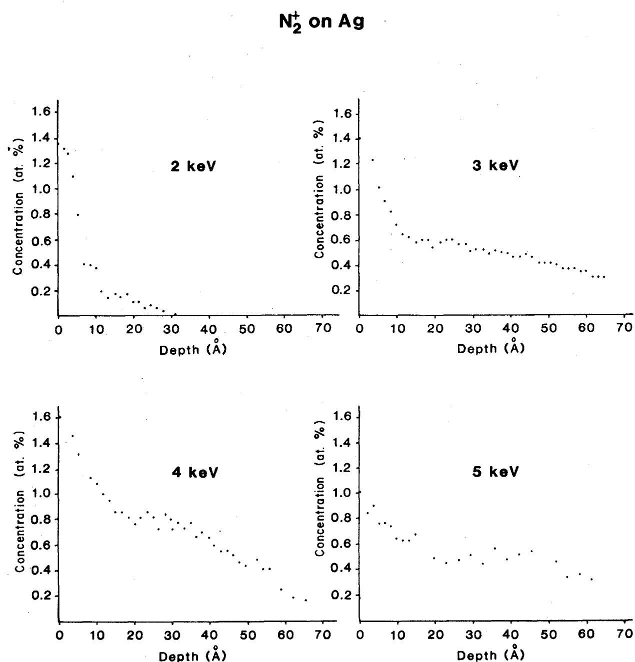

FIG. 3. Range distributions of 2–5-keV nitrogen ions in silver. The ion fluence for all of the distributions is about 5×10^{15} ions/cm^2.

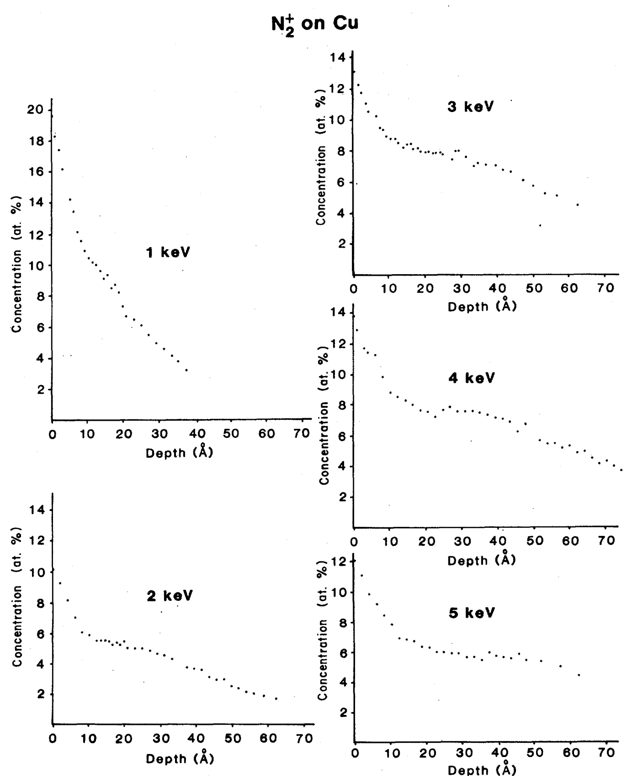

FIG. 4. Range distributions of 1–5-keV nitrogen ions in copper. The ion fluence for all of the distributions is about 5×10^{15} ions/cm^2.

imum is also moving to greater depth with increasing energy as is predicted by Sigmund[6] and Schiøtt.[5]

The values of the measured projected range vary from about 15 to 40 Å. Unfortunately, there are no available calculated values for the mean range of nitrogen ions on silver and copper for this range of energy (1 to 5 keV) which can be directly applied to the experimental data of Figs. 3 and 4. The closest values for mean range in the Winterbon tables[3] that could be compared to the present N_2 on silver data are those for carbon on silver. These are a factor of 2 larger than the values measured in this experiment. The very recent calculations of mean range reported by Littmark and Ziegler,[4] to be more appropriate at low values of reduced energy, either give the range values for very light ions (H and He) in various elements, or the calculations are done at relatively high energies (200 keV/amu). Neither case directly addresses the present work. As a result, we shall apply the LSS theory[1] as discussed by several authors[5,6,12] for comparison with our experimental data.

Figures 5 and 6 show the energy dependence of the secondary N_2^+ peak in copper and silver, respectively, as

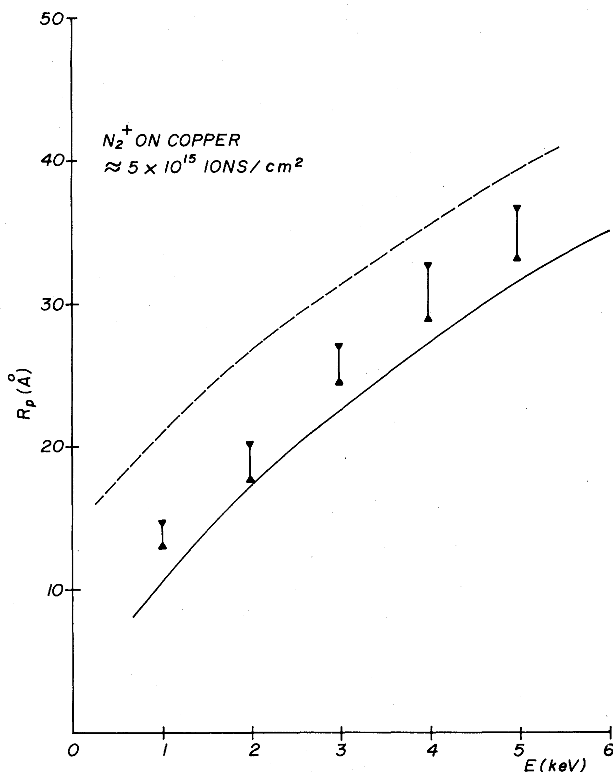

FIG. 5. Energy dependence of the projected range R_p of 1–5-keV nitrogen ions in copper compared with the predictions of Schiøtt (Ref. 5) (solid curve) and Winterbon, Sigmund, and Sanders (WSS) (Ref. 12) (dashed curve). In using WSS the conversion from total range to projected range was performed on the basis of Fig. 5 in Ref. 12, where values are calculated for $m=\frac{1}{2}$ and $\frac{1}{3}$. We have used the values of R_p for $m=\frac{1}{3}$ multiplied by 0.9 to account for the lower m values ($m=0.2$) corresponding to Lenz-Jensen interaction used for the total range calculation (Ref. 18).

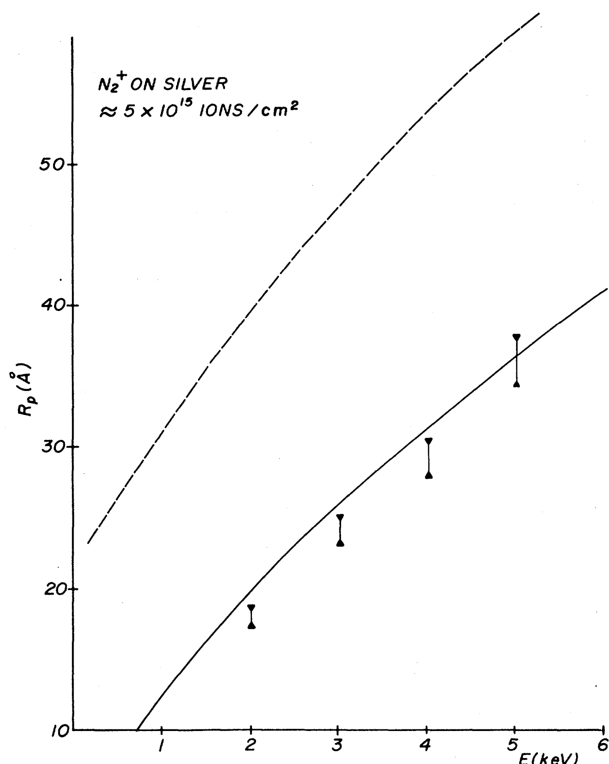

FIG. 6. Energy dependence of the projected range R_p of 2—5-keV nitrogen ions in silver compared with the prediction of Schiøtt (Ref. 5) (solid curve) and WSS (Ref. 12) (dashed curve). The calculation method are those described in Fig. 5.

extracted from the data of Figs. 3 and 4 by curve-resolution technique. The LSS theory[1] predicts an E^{2m} dependence for the mean projected range. With values of m in the range 0.2—0.3 the experimental results for both copper and silver are in good agreement with this prediction.

It is seen from Figs. 5 and 6 that the energy dependence of the experimentally determined projected ranges compares well with that predicted by theory. However, the projected range values as determined by the method of Ref. 12 are generally higher than experiment and those determined by the method of Ref. 5. This may be due to the different mass-ratio dependency of the conversion factor in calculating the average projected range from the total range in the two methods.

The surface localized peak is a new feature in the range distribution as compared to the theory and is not readily explainable. A number of possibilities come to mind and we will attempt to comment on each of them.

The sharp increase of the nitrogen concentration near the surface of the copper and silver samples could be an indication of chemical reactivity between the nitrogen and copper and silver at the surface. The AES peak shape of nitrogen in the case of N_2^+ on copper indicates two extra small features at 384 and 395 eV in addition to 355-, 367-, and 389-eV peaks corresponding to elemental nitrogen. These features could be a sign of some chemical reaction between nitrogen and copper. The state of nitrogen in silver, however, is similar to elemental nitrogen, indicating no or very weak chemical reaction between nitrogen and silver. It should be noted, however, that since energies of formation of such compounds are a few eV/molecule to a few tens of eV/molecule,[13] the effect of such a reaction channel on the stopping power for the incident several-keV ion may only be minimal. The heat of adsorption of nitrogen on copper and silver is also small. In the case of silver, for instance, it is ≈5 kcal/mol (Ref. 14) which is very weak and hence nitrogen is not expected to be strongly interacting with silver.

Another point to consider with respect to diatomic or molecular-ion implantation is the possible disproportionation of energy between the two atoms upon dissociation near the surface.[15] This could result in a low-energy and high-energy ion at the surface depending on the collision parameters. A surface peak may occur as a result. Re-

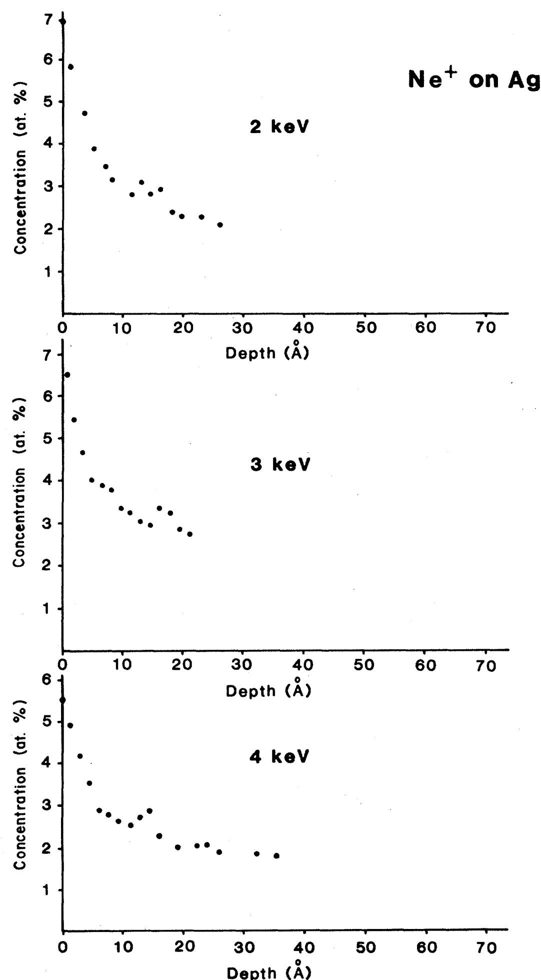

FIG. 7. Range distributions of 2—4-keV Ne^+ ions in silver. The ion fluence for all distributions is about 1×10^{16} ions/cm².

cent calculational modeling of a diatomic impinging on a surface has concluded that little disproportionation of energy occurs;[16] however, to check this point as well as the preceding point on the effect of chemical reactivity, implantation of Ne^+ into silver was performed. The features of the distributions are similar to those of N_2^+ on silver and copper (Fig. 7). Specifically, the surface peak is present even in the absence of any chemical reaction between the incoming ion (Ne^+) and host atoms (Ag). In addition, as Ne^+ is a monatomic ion the disproportionation argument cannot apply; nonetheless, the surface peak is still present. The secondary peak, however, is not as pronounced for Ne^+ as in the N_2^+ case due to the fact that even at a 10^{16} ions/cm^2 Ne^+ fluence the density of neon atoms remaining in the target is at a level close to the sensitivity limit of the spectrometer.

The surface peak could also be due to the recession of the surface due to sputtering during ion implantation resulting in piling up of the ions near the surface region. The surface peak in this case would be expected to be fluence dependent (absent for very small fluences and extremely prominent at large fluences). Figure 8 shows the fluence dependence of the 3-keV nitrogen distribution in copper. The fluence in each distribution was determined

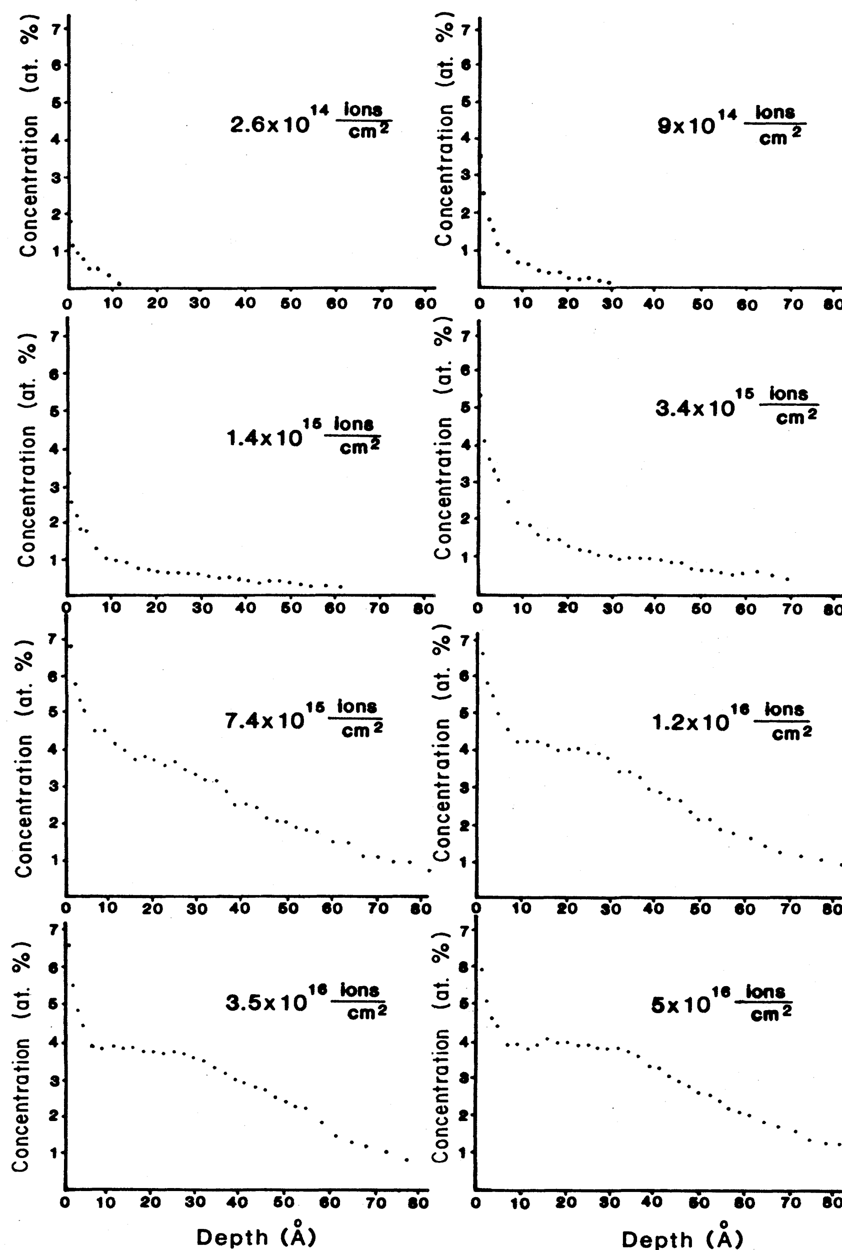

FIG. 8. Fluence dependence of the distribution of 3-keV nitrogen ions in copper.

by means of monitoring the ion-beam profile with narrow slit (0.8 mm) Faraday cup for beam area measurement and recording the ion-beam current and the time of the implantation. The presence of the surface peak in each distribution is clearly observed and eliminates the surface-recession or ion pile-up mechanism as being the cause of the surface peak. The area under the distribution curves follows the increase in fluence to within 10% up to a fluence about 10^{16}. At these high fluences the sputtering of the surface during the implantation results in saturation phenomena for the implanted ions as the area under the distribution almost remains constant (Fig. 8). At these high fluences the secondary peak of the distribution is more pronounced due to the larger number of implanted atoms present and also the tail of the distribution extends deeper into the target due to the knock-on effect during ion implantation.

During the sputtering of the samples with argon for depth profiling, the surface of the samples are damaged with possible resultant generation of surface relief, especially considering the fact that polycrystalline substrates have been used. Since the sputtering and the depth profiling are done at different angles, roughness at the surface of the samples could be the cause of the observed surface localization. To clarify this point, experiments were done on a polycrystal and a well-oriented, highly polished, low-defect (111) surface of a single crystal of copper (monatomic steps every approximate 35 Å as determined by low-energy electron diffraction). The ion implantation was done at 5 keV. The range distributions in both samples are shown in Fig. 9. The features of the two distributions are quite similar with no change in the observed surface peak. This result eliminates the possibility of surface roughness contributing to the observed surface peak.

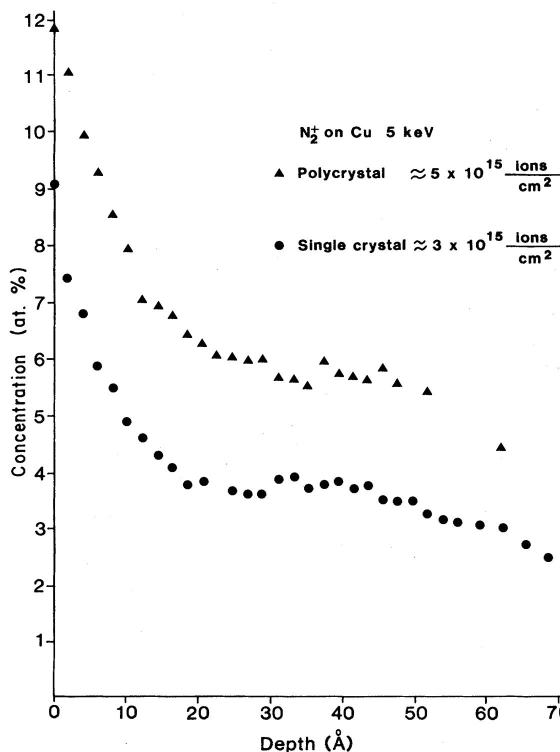

FIG. 9. Range distributions of 5-keV nitrogen ions in single crystal and polycrystalline copper.

Finally, the surface peak could be due to normal thermal diffusion of the implanted nitrogen atoms to the surface. This was monitored for both silver and copper by observing the time and temperature dependence of the intensity of the surface peak. The distributions reported above were all obtained at 80-K substrate temperature; however, measurements were also made during the course of the study at room temperature. It was noted for copper that there was little difference in the distributions at the two temperatures and no difference as a function of time over a period of several hours, at least an order of magnitude longer than the time it took to measure the distributions. For silver, on the other hand, normal diffusion of nitrogen was observed at room temperature both in the form of distribution different from the one measured at 80 K and in the form of changes in the measured distribution on time scales of the order of several minutes. At 80 K in silver, however, no change in measured distribution was observed over time periods of several hours indicating little or no contribution of normal thermal diffusion to the observed surface peak.

The above inspection of the surface-localized peak confirms this peak as part of the ion distribution readily observed under the conditions of low-incident primary-ion energies.[17] However, the nature of the surface peak is not yet clear. It could be due to the strong reflection of light ions from the surfaces of relatively heavy targets at low energies,[18,19] or it could be due to other factors such as radiation-enhanced diffusion.[20,21] These possibilities are currently being studied.[22,23]

CONCLUSION

The range distributions for the first time have been determined for 1-to-5-keV nitrogen ions implanted in copper and silver. The distributions show a high density of nitrogen near the surface along with a deeper lying secondary peak followed by a long tail into the target material. The position of the secondary peak as well as its energy dependence compares well to that predicted for the projected range peak by LSS theory as adapted by Schiøtt for such a low incident ion energy regime. The surface localized peak is not yet well understood; however, it has been shown not to be an artifact of the experimental technique or due to chemical interaction of species.

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