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Helium, neon and argon desorption from copper

E Kautto, J Kuhalainen and M Manninen

Department of Physics, University of Jyväskylä, Box 35, FIN-40351, Jyväskylä, Finland

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Abstract. We have used the thermal desorption method to study helium, neon and argon impurities in copper. Four different peaks are analysed from the helium desorption spectrum. Neon and argon spectra are more difficult to interpret. A new interpretation of the clear peaks of these spectra is given.

1. Introduction

Ion implantation followed by thermal desorption is a method for studying the energetics of rare gases in solids [1–3]. The experiment consists of the following steps: (i) a perfect, well annealed single crystal is bombarded with impurity ions; (ii) the sample is heated, usually at a constant heating rate, and the desorbing atoms are monitored by a mass spectrometer; and (iii) after the measurement the sample is usually annealed at high temperatures so that it can be used in further experiments.

Another variation of the method is helium probing [4]. In this case crystal defects are first created in the sample, for example by irradiation with heavy ions. After that helium is injected into the sample at energies so small that no further defects are created. Helium is trapped quite effectively by existing defects, and the desorption experiment gives information on the helium binding energies at defects.

The desorption spectrum can be analysed in most cases using the kinetic model [5, 6]:

$$\frac{dN}{dT} = -\frac{\nu}{\mu} N(T)^m \exp(-E_D/k_B T)$$

where N is the number of atoms in the sample, ν is the vibration frequency, μ is the heating rate, and E_D is the activation energy. In the case of gas desorption from solids, the reaction order is usually one ($m = 1$). The frequency constant is usually assumed to be independent of the temperature.

Classically, this model describes a trapped impurity atom which is vibrating in the defect and tries to escape over a potential barrier with a height of E_D [3]. When the peak analysis has been done with this model we have obtained a frequency factor and an activation energy for the desorption. The model also gives information on the concentration of vacancies in the solid, although this cannot be obtained straightforwardly, since there can also be multiply filled vacancies at least in the case of helium spectra.

In the present paper we report on measurements of helium, neon and argon desorption from copper. In the case of helium, we can determine activation energies, and the interpretation for several trapping sites is given. In the case of neon and argon, the situation is more difficult, and we give a new interpretation for the double peak seen at low implantation energies.

2. The experimental method

The facility used in this work has been described in detail in reference [8]. Here we give only a short description of the experimental facility.

The size of the sample used in this work is 10 mm × 10 mm × 1 mm. It was prepared by Metal Laboratory of Outokumpu Copper Incorporated. The surface was finished by mechanical polishing followed by an electrolytical polishing procedure. The purity of the sample was 99.999%. The surface orientation of the crystal was determined by using x-ray diffraction, and found to be accurately [340]. Before starting the measurements the sample was sputtered with argon and heated several times to 1000 K to remove argon impurities. Finally, some micrographs were taken using an atomic force microscope, to check the overall smoothness of the surface.

During the measurements, two different ion sources were used. Most of the measurements were done with a gas ion source connected to a thermal helium desorption spectrometer facility [8]. This gas ion source is not differentially pumped and it does not have mass analysis either. The energy of the ion beam can be varied from 100 eV to 3.0 keV. The beam of the gas ion source can have impurities as well as multiply charged ions. However, this is not a serious problem since these impurities are a minor part of the beam. This ion source was used mainly for helium implantation purposes. The other ion gun is an electron cyclotron resonance (ECR) ion source which is the main ion source of the local cyclotron [3, 8]. The ECR ion source can produce a large variety of ion beams with energies up to 100 keV. With this ion source it is also possible to produce different isotopes from selected elements. For example, in this work we have also used ^3He beams. Most of the Ar and Ne experiments, some of the ^4He and all of the ^3He experiments were done with the ECR ion source. The two ion sources produced similar results for helium.

In the desorption measurements, the temperature of the sample is increased at a constant rate, usually 1 K s⁻¹. The heating cycle is computer controlled. The temperature measurement is done using a thermocouple. Cooling of the sample is achieved with a cold finger filled with liquid nitrogen. In practice, the measurement can be started from 200 K. The desorbing gas was measured with a quadrupole mass spectrometer. The necessary ultra-high vacuum was achieved with a turbomolecular pump. A typical total pressure in the system is 10⁻⁸ Pa, and the background pressure of helium is about 10⁻¹⁰ Pa.

3. Results

3.1. Helium in copper above room temperature

The behaviour of helium in copper was studied by taking a large set of measurements, in which the copper sample was bombarded with a He beam using energies from 0.1 keV up to 10 keV, while the doses were in the range of 10¹² to 10¹⁴ ions cm⁻². The angle of the helium beam was 30° with respect to the normal of the surface. The bombardments were done using the gas ion source for low energies and the ECR ion source for high energies. The helium release was measured with the mass spectrometer while the sample was heated from 300 K to 900 K at a heating rate of 1 K s⁻¹. Figure 1 shows the results. Visible peaks are labelled with G, H, X, and I; this notation is adopted from Buters *et al* [9].

The peak labelled H can be associated with helium released from monovacancies. The temperature of this peak is the same in all cases, and its intensity increases with the dose. The H peak can be seen when the helium energy is higher than about 0.5 keV. It is the dominant peak in all of the measured spectra, and it is clearly caused by helium trapping

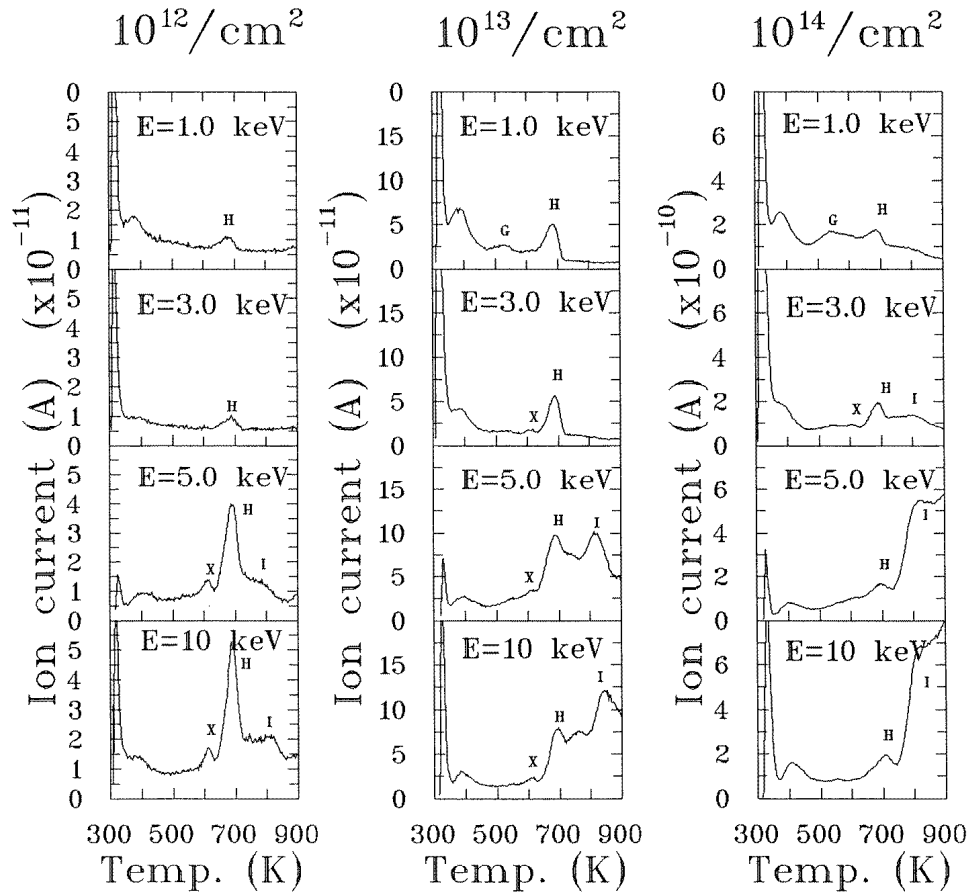


Figure 1. Spectra for helium desorption from single-crystalline copper. The irradiation doses are 10^{12} to 10^{14} ions cm^{-2} and the energies are 1–10 keV. The angle of the beam was 30° with respect to the surface normal, and the heating rate is 1.0 K s^{-1} in all cases. The peaks are labelled according to reference [9].

at monovacancies.

When the dose increases, we see three new peaks labelled G, X, and I. The peak labelled X is most clearly visible when the energy is in the range from 5 keV to 10 keV and doses are small. However, it is always a minor peak at the shoulder of the H peak. The suggested reason for the presence of this peak is helium release from HeV_2 where V_2 stands for a divacancy. Arguments in favour of this suggestion are as follows. The peak intensity increases when the energy increases, but the peak is small in every case. This is in agreement with the fact that when the energy increases there are more divacancies available. The calculated binding energies for one helium atom released from a divacancy are close to the calculated energy needed to release a helium atom from a monovacancy [10]. This is in agreement with the experimental result that the X peak is close to the monovacancy peak. The X peak cannot be associated with multiple filling of a monovacancy, because the peak is already seen at low doses, when there should not be multiple filling.

Another clear peak in the spectra is the G peak. This peak is most clearly visible

when the irradiation energies are low, and it disappears with increasing energy. At low energies, the intensity of this peak rises rapidly with increasing radiation dose. This means that the trapping rate associated with the G peak is strongly dependent on the dose. The suggested mechanism for this peak is the production of a doubly filled monovacancy. We also performed experiments in which vacancies were produced using a 1.0 keV helium beam followed by helium implantation with the energy 0.1 keV, which is too low to produce further vacancies. After that, the sample was annealed at 400 K to eliminate surface contaminants, and it was cooled down to room temperature. Finally, desorption spectra were recorded. These experiments also indicated that the G peak is associated with the scheme



The G peak is notably wider than other first-order peaks. The reason for this is probably that the G peak is caused by the combination of helium releases from doubly and triply filled vacancies. The energies of the two processes are expected to be close to each other. Peak I is seen only with the highest doses and with the highest energies, so we can assume that the origin of that peak lies in more complex defects in the lattice, most probably vacancy clusters.

Peak analysis methods based on the kinetic equation are explained in detail in reference [7]. The main peak, in all of the spectra, is the H peak. The shape of that peak is quite accurately the same in all of the spectra, and peak analysis done with different methods gave an activation energy of $E_D = 2.0$ eV and a vibration frequency of 10^{13} s^{-1} . All of the analysis methods give the activation energy quite accurately, but the frequency is more sensitive, since it depends exponentially on the activation energy, and a small variation in E_D leads to a large variation in ν .

Due to the overlaps and the small sizes of the G and X peaks, it is difficult to determine their activation energies and vibration frequencies using more sophisticated peak analysis methods. We can, however, estimate energies if we assume the vibration frequency to be the same as for the H peak. The peak energies can then be calculated from the peak maximum temperatures and vibration frequencies. The peak maximum temperatures are $T_G = 540 \pm 2$ K and $T_X = 610 \pm 2$ K, and, assuming a vibration frequency of $1.0 \times 10^{13} \text{ s}^{-1}$, the activation energies are $E_{D,G} = 1.52$ eV and $E_{D,X} = 1.73$ eV.

3.2. Desorption of ^3He

In a simple classical model the escape rate of the helium atoms from the defects is proportional to the vibration frequency of the atoms in those defects. In a harmonic oscillator model, the vibration frequency is inversely proportional to the square root of the mass of the atom ($\nu \propto m^{-1/2}$). The classical treatment then predicts that the vibration frequency is inversely proportional to the square root of the mass of the atom. If now ^4He is replaced with ^3He , the frequency increases by a factor $(4/3)^{1/2} = 1.15$. If the same holds true down to zero-point frequencies, then the zero-point energy of ^3He is also slightly larger than the zero-point energy for ^4He , and the corresponding dissociation energy is smaller. If we assume that the activation energies are of the same order in the two cases, we can suggest that the isotope effect shifts the ^3He peaks to a lower temperature. This is however only a crude approximation. The assumption that the activation energies are the same is justified, since the energetics is governed by the electron densities of helium atoms, and in principle they are the same for the two isotopes.

Experiments that have been done with ^3He show a few differences as compared to ^4He

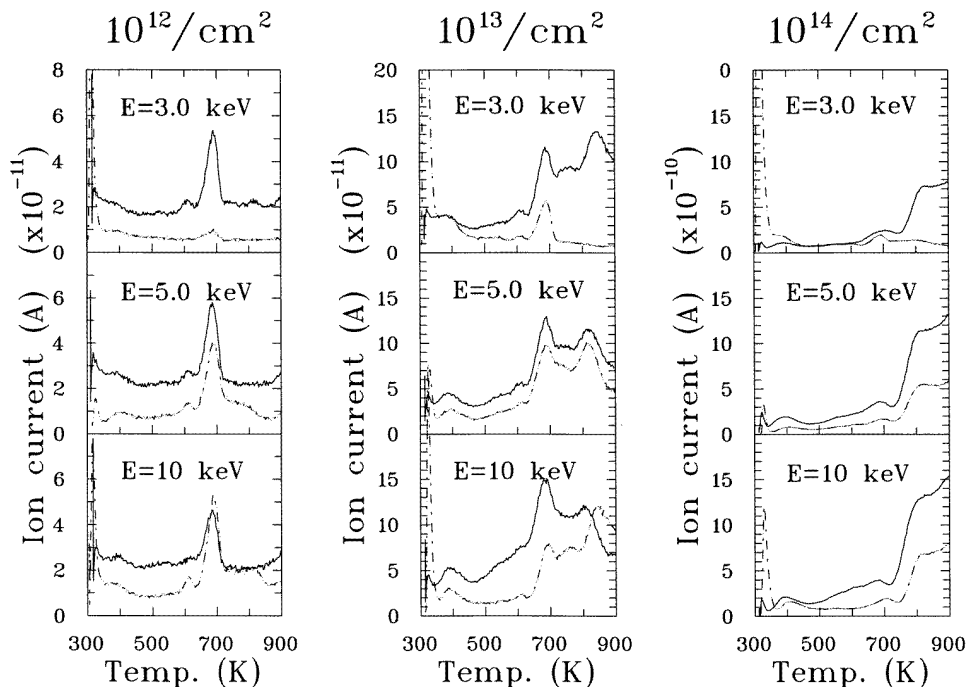


Figure 2. Measured ^3He (thicker line) and ^4He (dashed line) spectra. There are only minor differences between these spectra. In all cases, the peak maximum temperature is 2 K higher in the ^4He case. All of the peaks are measured for the heating rate 1 K s^{-1} [3].

measurements (figure 2). Firstly, the background level is higher in the ^3He experiments. The probable reason for this is that the turbomolecular pump is not so effective for ^3He as for ^4He , since it has a higher thermal speed. Another notable difference is that the intensities are higher for ^3He peaks as compared to the corresponding ^4He peaks. There is no evident reason for this effect, since the total irradiation doses are the same. Figure 2 shows measured ^3He and ^4He desorption spectra for the same window. These show that the temperatures of the ^3He peaks are indeed lower. However, the accuracy of the temperature measurement is not more than this shift in the peak position. When the ^3He peaks were analysed, we observed that the vibration frequency is $2.3 \times 10^{13} \text{ s}^{-1}$, and the activation energy is 2.0 eV, as it was in the case of ^4He . The observed peak separation of 2 K fits with classical predictions related to the isotope effect. One must also note that the accuracy of the temperature measurement is not more than 2 K, so the peak shift is within experimental error.

3.3. Low-temperature measurements

The main motivation for starting the measurements from lower temperatures was the need for information on the migration energies. In these experiments the sample was cooled down to 200 K. When the desired temperature was reached, the sample was bombarded with a dose of $10^{13} \text{ He}^+ \text{ cm}^{-2}$ using different energies. After irradiation, the sample was heated up to 900 K at the rate of 1 K s^{-1} while the helium release was monitored with the mass spectrometer. The irradiation at low temperatures leads to higher intensities in the

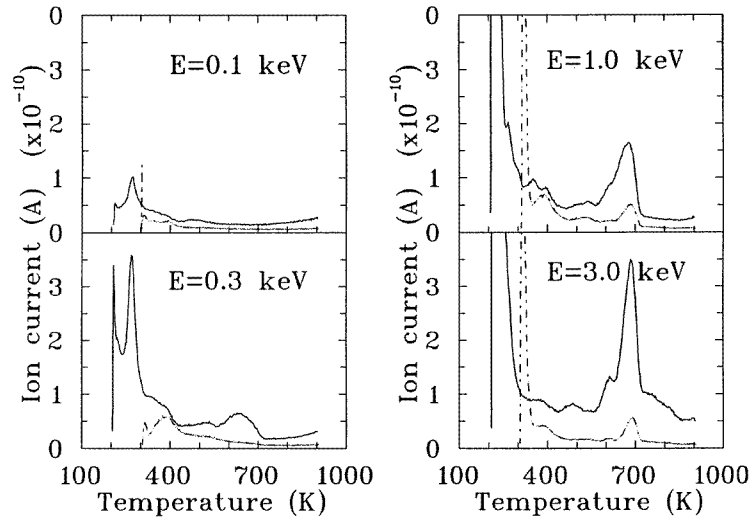


Figure 3. Results for low-temperature measurements. In these measurements the single-crystalline copper was bombarded with a helium beam while the temperature was 200 K. The dashed line shows room temperature measurements [3].

H and X peaks than the room temperature irradiation. Figure 3 shows these measurements. This is expected, since vacancies are not so mobile at low temperatures, and, consequently there are more vacancies available in the sample. Therefore there are also singly filled divacancies, which are the expected origin of the X peak. The result also indicates that for the room temperature measurements a major fraction of the vacancies are annihilated with self-interstitials, or they escape to the surface before being decorated with helium.

The calculated migration energy for helium in copper is 0.5 eV [13]. If the energy of the helium beam is 3.0 keV, then the penetration of helium atoms is around 100 ± 50 atomic layers, as estimated from TRIM calculations [15]. If the helium release is described using a one-dimensional diffusion model, we can estimate that the diffusion peak maximum should be at 249 K. This is close to the second peak that is seen at around 270 K in figure 3.

3.4. Neon and argon in copper

Heavier gas atoms, like those of neon and argon, transfer energy to target atoms more efficiently than helium. The penetration depths are smaller and more defects are created. The migration energies are expected to be much higher than that of helium.

All measurements with heavier gases were done in the same fashion as the helium desorption experiments. The sample was also cooled down to 200 K in these experiments. Figure 4 shows the results for argon. The results are quite different from the helium results. All of the peaks seem to be wider. It is not possible to apply the tested peak analysis methods, since the order of reaction is not known, and it is possible that the vibration frequency is temperature dependent. Another visible effect is the double peak seen with low-energy irradiation. The high-temperature peak seems to disappear when the irradiation dose is lowered to 1.0×10^{12} ions cm^{-2} . This is not the case for the low-temperature peak. In fact, the same kind of behaviour has been observed also in nickel measurements by Edwards [11]. He gives the explanation that the low-temperature peak is related to surface

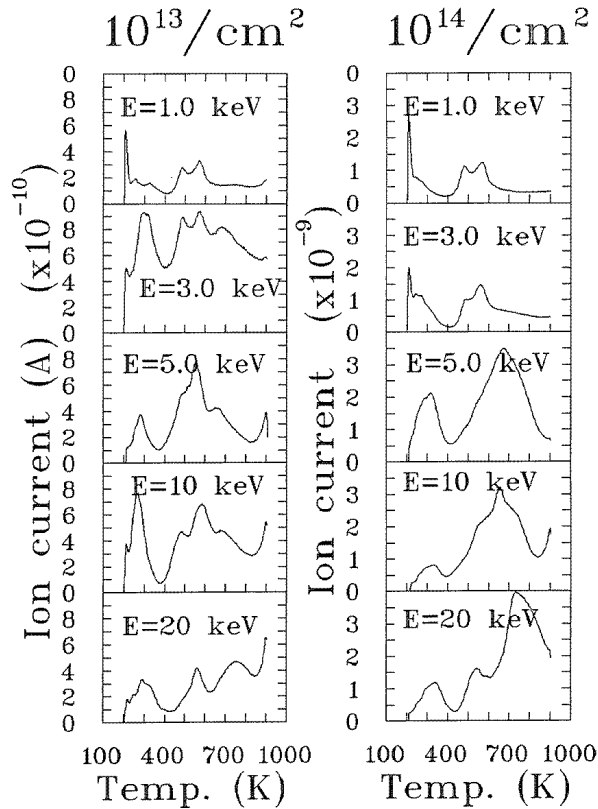


Figure 4. Spectra for argon desorption from copper. These irradiations were done at 200 K. The heating rate is 1.0 K s^{-1} in all cases [3].

trapping, while the high-temperature peak is due to substitutional traps located deeper in the crystal. Taking into account the different heating rates, the behaviours of argon in nickel and in copper are very similar. Also, other authors have proposed that in the case of heavier gases there are more peaks, which are due to gas desorption from different atomic layers [12]. We tried to confirm this by doing experiments in which the sample was bombarded using different angles of incidence. We did not observe peak intensity variation with the angle, so this question remains unresolved.

Another explanation for the double-peak structure is the occurrence of singly and doubly filled vacancies. According to our theoretical estimations, the doubly filled monovacancy (with argon) is not favoured [13]. Also, when compared to helium experiments, this double peak is at a lower temperature than the monovacancy peak in the helium case. This would mean that the activation energy for argon is lower than that for helium. This is in disagreement with our calculation, which shows that the energies for argon are much higher than those for helium. Also, migration energies are somewhat higher for argon [13].

A third explanation for the double peak is the existence of singly and doubly filled divacancies. This seems to be a reasonable explanation, since activation energies for diffusion are lower in the case of divacancies. However, there is no direct experimental or theoretical evidence for this.

The high-energy argon spectra also show wide peaks at high temperatures. In some

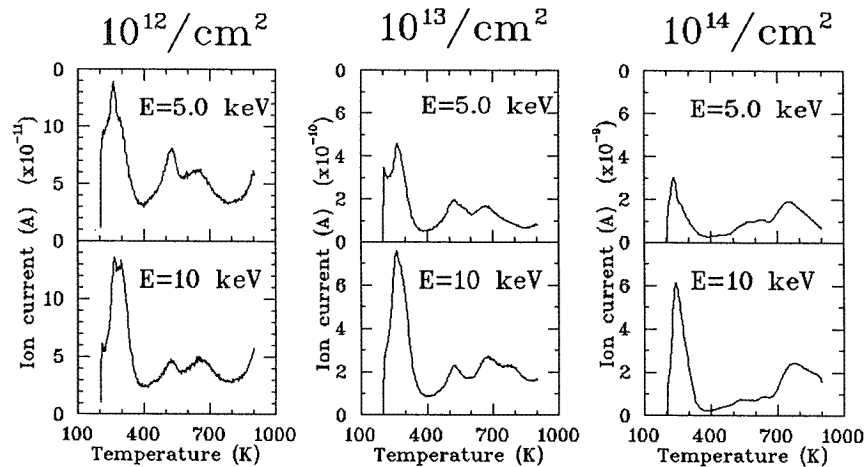


Figure 5. Spectra for neon desorption from copper. The basic features of these spectra are essentially the same as those of the argon desorption spectra (figure 4) [3].

cases there is also a rising edge, which might be due to diffusion. In any case, these higher-temperature peaks are strongly dependent on the dose and on the irradiation energy, so they are most probably related to larger defects, such as vacancy clusters.

The desorption of neon from copper is quite similar to argon desorption. There are only minor differences in the spectra. In the case of neon there is a strong peak in the low-temperature part, as seen in figure 5. The maximum of the peak is at around 250 ± 20 K. A possible explanation for this peak is interstitial diffusion. The diffusion model gives a migration energy of 0.5 eV. This might not be the only mechanism, since the theoretical estimate for the migration energy is much higher, $E_m = 0.8$ eV [13]. In fact these calculations showed that the migration energy of argon is smaller than that of neon. The measurements also indicate that the first peaks in the argon spectra are at lower temperatures than in the case of neon. Another explanation for the first peak is that defects are located in the first or in the second atomic layer.

The double peak that is observed in the argon spectra is clear also in the neon case. In the case of neon, the peak temperatures are 520 K and 660 K, whereas for argon they are 485 K and 570 K, when the heating rate is 1 K s^{-1} . In both cases the high-temperature peak is more strongly dependent on the irradiation energy as well as on the dose. At higher temperatures than that at which the double peak occurs, there is a peak which becomes visible when the bombarding doses are of the order of 10^{14} ions cm^{-2} . This peak can be associated with larger defects. The unexpected result is that the peaks in the neon spectra are at higher temperatures than in the argon case. This means that the trapping energies are higher for neon. This result is in agreement with our theoretical results [13], that the trapping energy of neon in a vacancy is much higher than the trapping energy of argon. However, the double peaks are in such a temperature range that their activation energies cannot be associated with trapping at monovacancies.

In the case of neon in particular, the double peak cannot be explained in terms of desorption from different atomic layers. For example, when the irradiation energy is 10.0 keV, the mean penetration depth is around 50 atomic layers, when the angle of incidence is 30° . In this case, the first few atomic layers cannot give a significant contribution

to the spectra. Our recent molecular dynamics calculations (to be published) show no significant effects near the surface. A simple diffusion model indicates that the mean time of diffusion through 50 atomic layers is around $10 \mu\text{s}$, indicating that it is nearly impossible that the high-temperature peak of the double peak is caused by diffusion-controlled desorption. The likeliest explanation is again that these peaks are related to singly and doubly filled divacancies.

3.5. Helium probing

As noted earlier, heavier atoms can form more complex defects because of the larger relaxations around the defect, and because of the stronger interactions with local electron density variations. For this reason, we tried to study these effects more carefully using the helium probing technique. The copper sample was first irradiated with a neon or argon beam, and thereafter low-energy helium was injected into the sample. It is assumed that helium is trapped quite effectively by defects that are already in the sample. In the first experiments, irradiations were carried out at room temperature, and the helium beam energy was 3.0 keV. The same energy was used for argon.

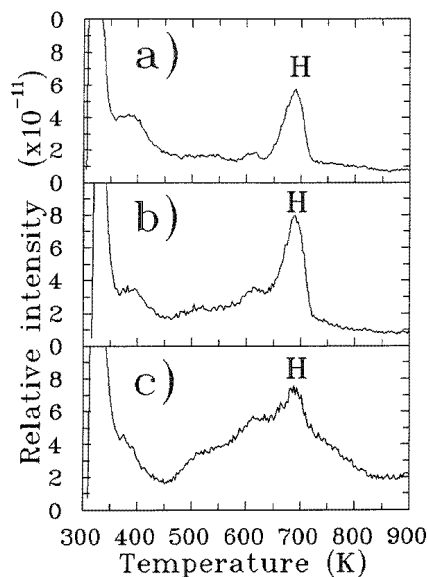


Figure 6. Spectra for the helium desorption from copper when the sample was preirradiated with a 3.0 keV argon beam. The argon doses are (a) none, (b) 10^{13} ions cm^{-2} , and (c) 10^{14} ions cm^{-2} . The helium doses are 10^{13} ions cm^{-2} in all cases [3].

In the case of argon preimplantation, we observed strong distortion of the helium spectra (figure 6). The monovacancy peak is clearly visible for pure helium bombardment, but in this case of preimplanted argon a wide structure is observed in the temperature range 500–700 K. However, the monovacancy peak is still as intense as it is for the case without preimplantation. The most probable explanation for these new broad peaks is helium release from argon–vacancy clusters which are near the surface. The same kind of phenomenon is also obtained in the case of indium-implanted copper [14].

When the argon implantation was done after the helium bombardment, different effects

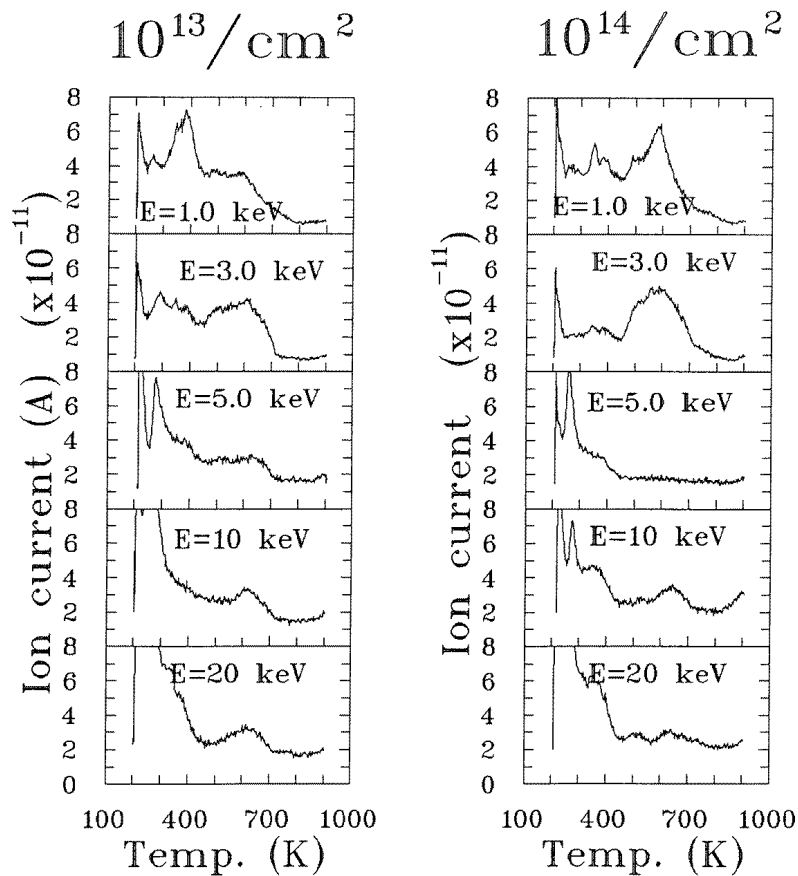


Figure 7. Spectra for the helium desorption from copper when the copper sample is prebombarded with argon. The helium beam energy was only 0.3 keV. The heating rate was 1.0 K s^{-1} .

were obtained. In this case the increase of the argon dose quickly reduces the helium H peak. When the argon dose is of the order of $10^{14} \text{ ions cm}^{-2}$, the H peak disappears. The reason for this kind of behaviour is quite clear. When argon is implanted in copper, self-interstitials of copper are introduced and they are mobile at these temperatures. Helium atoms that are 'kicked out' by those self-interstitials escape to the surface before they can be detected. Also, helium atoms that are trapped near the surface layer are 'kicked out' by argon bombardment.

The actual helium probing experiments were done with much smaller helium energies. In these experiments we bombarded the sample with a 1.0–20.0 keV argon beam, and after that we injected helium with an energy of 0.3 keV. The argon doses were varied within the range 10^{13} – $10^{14} \text{ ions cm}^{-2}$, and the helium dose was $10^{13} \text{ ions cm}^{-2}$. The sample was also cooled down to 200 K in these experiments. Figure 7 shows the results. The most striking effect is the absence of an H peak. This indicates that there are no free vacancies in the sample after the argon bombardment.

In general the spectra (which are reproducible) show a complicated dependence on the argon energy and dose. Much more experimental and theoretical work is needed for

Table 1. Peak temperatures and dissociation energies for the main peaks observed for helium, neon and argon desorption.

Impurity	Peak	Temperature (K)	Process involved	Energy (eV)
⁴ He	H	700	HeV → He + V	2.0
⁴ He	G	540	He ₂ V → He + HeV	1.52
⁴ He	X	600	HeV ₂ → He + V ₂	1.73
³ He	H	700	³ HeV → ³ He + V	2.0
Ar	—	200	Migration	—
Ar	—	485	ArV ₂ → Ar + V ₂	—
Ar	—	570	Ar ₂ V ₂ → Ar + ArV ₂	—
Ne	—	250	Migration	—
Ne	—	520	NeV ₂ → Ne + V ₂	—
Ne	—	660	Ne ₂ V ₂ → Ne + NeV ₂	—

achieving an understanding of the escape of helium from the crystal containing defects before helium probing can be used as a standard tool for studying defects in solids.

4. Conclusions

The experiments presented in this paper show that thermal desorption spectroscopy can provide a lot of information about the behaviour of helium in metals. In helium spectra the most clearly visible peak in all cases is the monovacancy peak (labelled H). Peak analysis using all known methods gives an activation energy of $E_D = 2.0$ eV, while the corresponding frequency factor is $\nu = 1.0 \times 10^{13} \text{ s}^{-1}$. The peaks labelled with G and X were associated with a doubly filled monovacancy and a singly filled divacancy respectively. The dissociation energies were $E_{D,G} = 1.52$ eV and $E_{D,X} = 1.73$ eV. These energies were estimated from the peaks by assuming that $\nu = 1.0 \times 10^{13} \text{ s}^{-1}$, as it was in the case of the H peak. It is, however, not possible to analyse these peaks (G, X, and I) using more accurate methods, since they are either small or overlapping. Measurements with ³He indeed do show slight differences in the peak temperatures when compared with the ⁴He case. This agrees well with the simple predictions. Table 1 summarizes the main peaks in the spectra.

The neon and argon spectra were much more complex than the helium spectra. In both cases we obtained a double peak which cannot be due to impurity release from monovacancies, since the peak temperatures are not high enough for that. Earlier explanations for the double peak were related to desorption from different surface layers. We believe that this explanation is not correct. Our best explanation for the double peak is the existence of singly and doubly filled divacancies. The peaks are so broad that it is impossible to analyse them reliably using known analysis methods. Unexpectedly, the double peak appears at higher energies for neon than for argon.

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