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Isotopic effect in the formation of copper-ion clusters by neutral-argon-atom bombardment

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8-keV neutral argon atoms are used to bombard pure polycrystalline copper for production of ion clusters which are analyzed by a high-precision mass spectrometer. The odd-even alternations in the secondary emission of copper-ion clusters together with various kinds of heteroisotopic cluster ions are observed. For the first time the experiments have shown that the isotopic effect plays an important role in the formation of polyatomic cluster ions by sputtering.

In recent years the study of small metal particles which consist of only a few constituent atoms has drawn great attention because it allows one to have better knowledge of the early steps in metal formation. Also, the metal atomic clusters represent an unexplored state of matter, a state in between that of a metal and that of a gas, and may have unusual potential applications such as catalysts.[1,2]

An intriguing approach to producing metal clusters involves the ion bombardment of metal surfaces. The formation of secondary-metal-ion clusters containing several atoms has been observed to occur upon bombardment of solids with primary ions of kinetic energy on the order of a few to a dozen keV. The relative intensity of polyatomic ions has been found to be correlated with the crystal orientation of the metal surface[3] and with the electronic properties and thermodynamic stability of a particular sized cluster.[4]

We have carefully examined the emission of secondary-ion clusters of some metals, alkali halides, and semiconducting materials by several keV neutral inert-gas atom bombardments, and found great amounts of heteroisotopic cluster ions in most cases and isotopic effect in the formation of metal-ion clusters by sputtering. In this paper we will first discuss the copper-ion clusters.

The experiments were performed by VG ZAB-HS instrument (VG Atlanta Ltd.), combining high resolution and high sensitivity with facilities to carry out mass analyzed ion kinetic energy spectrometry (MIKES), working with fast atom bombardment (FAB), and double focusing mode. 8-keV neutral argon atoms as a bombarding beam were obtained through a charge-exchange process and deflection of remaining charged ions from the FAB gun composed of a saddle-field cold-cathode ion source. The instrument has a mass range of 2000 amu at 1 kV (we were working at mass range of 1000) and is capable of a resolution of up to 100000 (10% valley definition). The different masses are filtered in momentum analysis with a magnetic sector and then in energy analysis with an electrostatic sector.

A polycrystal copper with high purity was chosen to be the target and the incident angle between the primary beam and the surface of the sample was 30°, and the working pressure in the bombarding chamber was 3×10^{-6} mbar. The data were transferred to and analyzed by PDP11/250 computer (VG Atlanta Ltd). The computer program was written to select the intensities I_i of signals above the set noise level at time t_i and to integrate the energy spectrum for each species, obtaining the intensities of the clusters with same mass (in fact, the energy spectrum for each mass was sectioned with energy steps and values are summed up to have the yields of the clusters).

Figure 1 presents one of the mass spectra of the Cu sample by 8 keV argon atom bombardment with beam current 1 mA, and some mass numbers are identified as those of the corresponding copper cluster ions Cu_N^+ whose relative yields are obviously larger than their neighbors. Table I lists various kinds of copper ion clusters produced, their masses, and the relative SIMS yields which have been normalized to that of ion $^{63}Cu^+$. The relative yields for the clusters in Table I are the average values for several time measurements and the numbers in parentheses are the maximum deviations from the average values in each case. The sputtering yields for $^{63}Cu^+$ and $^{65}Cu^+$ (100.0% and 41.68%, respectively) are very close to their natural abundances of ^{63}Cu and ^{65}Cu (69.1% and 30.9%, respectively). The cluster Cu_2^+ contains three kinds of cluster ions with different masses: $^{63}Cu_2^+$, $(^{63}Cu_1\,^{65}Cu_1)^+$, and $^{65}Cu_2^+$ whose yields are 3.53, 3.66, and 1.21, respectively. For $N=3$, the clusters $^{63}Cu_3^+$, $(^{63}Cu_2\,^{65}Cu_1)^+$, and $(^{63}Cu_1\,^{65}Cu_2)^+$, as well as $^{65}Cu_3^+$, are found with unexpected pronounced peaks for $(^{63}Cu_2\,^{65}Cu_1)^+$ and $(^{63}Cu_1\,^{65}Cu_2)^+$ though the abundance ratio of $[^{65}Cu]/[^{63}Cu]$ is only 2/5 in the sample. For $N=4$ the yields of clusters $(^{63}Cu_1\,^{65}Cu_3)^+$ and $^{65}Cu_4^+$ are missing. Both Cu_5^+ and Cu_6^+ have three kinds of clusters while Cu_7^+ has four. It is interesting to note that we have obtained only cluster $^{63}Cu_8^+$ for $N=8$ and the cluster $(^{63}Cu_8\,^{65}Cu_1)^+$ for $N=9$.

In fact, these cluster ions Cu_N^+ can be grouped by homoisotopic clusters such as $^{63}Cu_2^+$, $^{65}Cu_3^+$, . . . , and heteroisotopic ones as $(^{63}Cu_1\,^{65}Cu_1)^+$, $(^{63}Cu_2\,^{65}Cu_1)^+$, ... We define intensity $I(N)$ for the yield

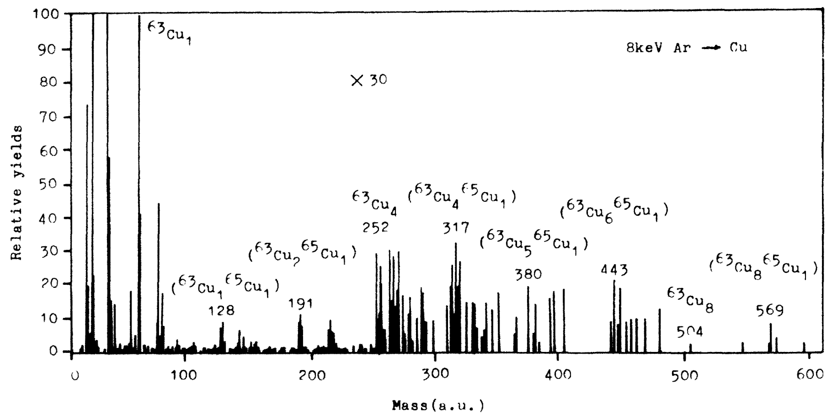

FIG. 1. SIMS spectrum of polycrystal copper by 8-keV argon atom bombardment.

summation of clusters Cu_N^+ with the same number of copper atoms and $I_{he}(N)$ for that of heteroisotopic cluster ions with same N. Therefore, the ratio $R = I_{he}(N)/I(N)$ can represent the isotopic effect in the formation of metal cluster ions by sputtering. Table II gives all values of $I(N)$, $I_{he}(N)$, and R, and Fig. 2 illustrates the changes of I and I_{he} as function of number of copper atoms per cluster N.

The following features are clearly seen from Tables I and II, and Fig. 2.

(1) All parameters I, I_{he}, and R show odd-even alternations versus N and are satisfied with the relations as

$$I(Cu_{2p+1}{}^+) > I(Cu_{2p}{}^+),$$
$$I_{he}(Cu_{2p+1}{}^+) > I_{he}(Cu_{2p}{}^+),$$
$$R(Cu_{2p+1}{}^+) > R(Cu_{2p}{}^+),$$

TABLE I. Various kinds of copper ion clusters produced by 8 keV argon atom bombardment.

Ion clusters Cu_N^+	Isotopes	Mass	Relative yields[a]	$I(^{63}Cu_m\,^{65}Cu_n)$[b]
Cu^+	^{63}Cu	63	100.0	0.706
	^{65}Cu	65	41.68(2.88)	0.294
Cu_2^+	$^{63}Cu_2$	126	3.53(0.45)	0.498
	$^{63}Cu_1\,^{65}Cu_1$	128	3.66(0.49)	0.415
	$^{65}Cu_2$	130	1.21(0.24)	0.086
Cu_3^+	$^{63}Cu_3$	189	8.90(1.24)	0.352
	$^{63}Cu_2\,^{65}Cu_1$	191	11.30(1.32)	0.493
	$^{63}Cu_1\,^{65}Cu_2$	193	8.50(1.00)	0.183
	$^{65}Cu_3$	195	1.25(0.22)	0.025
Cu_4^+	$^{63}Cu_4$	252	0.99(0.19)	0.245
	$^{63}Cu_3\,^{65}Cu_1$	254	0.36(0.08)	0.419
	$^{63}Cu_2\,^{65}Cu_2$	256	0.54(0.11)	0.043
Cu_5^+	$^{63}Cu_5$	315	0.34(0.05)	0.175
	$^{63}Cu_4\,^{65}Cu_1$	317	1.09(0.15)	0.365
	$^{63}Cu_3\,^{65}Cu_2$	319	0.63(0.08)	0.309
Cu_6^+	$^{63}Cu_6$	378	0.08(0.03)	0.124
	$^{63}Cu_5\,^{65}Cu_1$	380	0.20(0.05)	0.309
	$^{63}Cu_4\,^{65}Cu_2$	382	0.0	0.322
	$^{63}Cu_3\,^{65}Cu_3$	384	0.09(0.04)	0.178
Cu_7^+	$^{63}Cu_7$	441	0.30(0.05)	0.087
	$^{63}Cu_6\,^{65}Cu_1$	443	0.70(0.08)	0.254
	$^{63}Cu_5\,^{65}Cu_2$	445	0.27(0.05)	0.318
	$^{63}Cu_4\,^{65}Cu_3$	447	0.65(0.11)	0.221
Cu_8^+	$^{63}Cu_8$	504	0.08(0.03)	0.062
	$^{63}Cu_7\,^{65}Cu_1$	506	0.0	0.205
Cu_9^+	$^{63}Cu_9$	567	0.0	0.045
	$^{63}Cu_8\,^{65}Cu_1$	569	0.29(0.04)	0.163

[a]The data listed here are the average values of measurements taken several times and the numbers in parentheses are the maximum deviations from the average values in each case.

[b]Partial intensities of various ion clusters ($^{63}Cu_m\,^{65}Cu_n{}^+$) expected from statistics.

TABLE II. Isotopic effect in the formation of copper cluster ions by SIMS. Note: $I(Cu_{2p+1}) > I(Cu_{2p})$ (p is positive integer).

Ion cluster Cu_N	I	I_{he}	$R = I_{he}/I$ (%)
Cu(63)	100.0		
Cu(65)	41.68		
Cu_2	8.40	3.66	43.5
Cu_3	29.95	19.85	66.2
Cu_4	1.89	0.90	47.6
Cu_5	2.06	1.72	83.5
Cu_6	0.37	0.29	78.3
Cu_7	1.92	1.62	84.3
Cu_8	0.08	0.0	0.0
Cu_9	0.29	0.29	100.0

where p are the positive integers.

(2) Most heteroisotopic clusters have relatively large yields, especially for those that contain an odd number of copper atoms; for instance, cluster ions $(^{63}Cu_{2p}\ ^{65}Cu_1)^+$ have much more abundance than the others. When $N=9$ only heteroisotopic cluster ion $(^{63}Cu_8\ ^{65}Cu_1)^+$ is produced with the yield $I_{he}= 0.29$. From our experiments done so far we have never found any kind of copper ion cluster Cu_{10}^+ but have had the cluster Cu_{11}^+ which consists of $(^{63}Cu_9\ ^{65}Cu_2)^+$ with its relative yield of 0.17.

These indicate that (a) the secondary emission of heteroisotopic clusters are preferential and (b) the isotopic effect may play an important role in the sputtering process of copper metal by 8-keV Ar neutral atom bombardment since the relative intensity $I_{he}(N)$ and ratio R show well-defined alternation according to the parity of N.

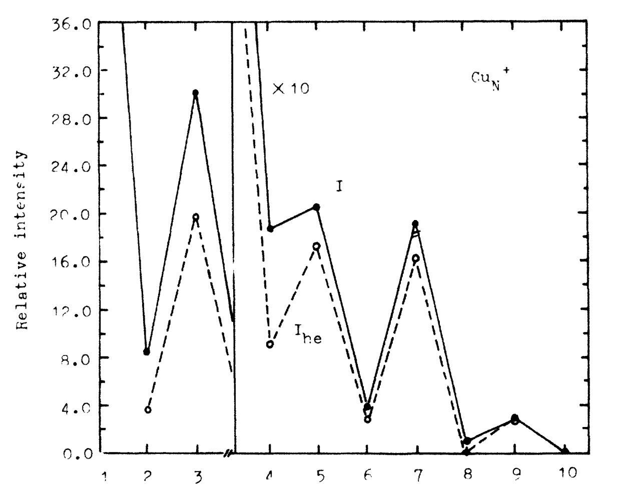

FIG. 2. The relative intensities of ion clusters Cu_N^+ and heteroisotopic cluster ions as function of number of atoms per clusters. I: relative intensity of all ion clusters Cu_N^+ with same number of atoms N. I_{he}: relative intensity of heteroisotopically atomic clusters with the same number of atoms N.

For many years the mass spectrum characters in secondary emission of ion clusters from alkali-metal, noble, and transition elements have been explained only by considering electronic properties of these materials in the frame of Hückel approximation.[5,6] In order to interpret odd-even alternation of the emission intensity in SIMS spectra of the metal ion clusters, Leleyter and co-workers[7,8] further proposed the linear-chain model for the copper-ion clusters to calculate the electron energy of a N-atom ionized cluster given by the energy of $N-1$ electrons, and obtain the binding energies of the copper cluster ions Cu_N^+, which exhibit an oscillating behavior in agreement with their experimental results.

However, there are two basic problems for this linear-chain model. (1) The optimal configurations of the ion clusters with several atoms are not always linearly structured, especially when N becomes large.[9,10] (2) It is difficult to explain SIMS spectra of some metal clusters such as Na_N^+ by this model.[11] Even in the case of copper cluster ions Cu_N^+ from our experiments the sputtering yields of homoisotope clusters $^{63}Cu_N^+$ do not show good odd-even alternation; for example, the relative yield of $^{63}Cu_4^+$ is greater than that of $^{63}Cu_5^+$ (see Table I). But when we take considerations of the intensities for the clusters of the same N and that for the heteroisotopic clusters, both $I(N)$ and $I_{he}(N)$ show perfect odd-even alternations, which cannot be explained by Joyes's linear-chain model.

Blaise[12] has suggested that the partial intensities of various ion clusters A_mB_n (here A and B represent two different isotopes of an element, m and n are their number of atoms, respectively), including a constant number $n+m$ atoms are proportional to the isotopic abundance of the cluster $A_mB_n^+$. He has obtained a general formula for the intensity of a cluster of two atomic species, which depends on the total sputtering yield, the structural factor as well as the ionization probability. The last column in Table I gives the partial intensities of various ion clusters $(^{63}Cu_m\ ^{65}Cu_n)$ (i.e., $N=m+n$) expected from statistics. Although the values result from a random distribution of atoms without taking the ejection and ionization processes into account, it implies that the isotopic abundance of the target material may strongly affect the secondary emission of molecular ions. Furthermore, in recent years many experimental results of secondary-ion mass spectrometry have demonstrated that there exists the isotopic fractionation of some elements such as Ca, Si, Mo, Cu, and U by sputtering, which is time dependent and associated with the composition and the crystallinity of samples, and has strong angular dependence even at noncrystalline materials.[13-15] Very recently, for instance, 27-keV Ar ions are used to sputter the amorphous Cu film and an obviously angular dependence of the emission ratio of ^{63}Cu and ^{65}Cu are observed.[16] When the emission angle is greater than 50°, the emission of the isotope ^{63}Cu is preferential. This kind of isotope fractionation of the sputtered materials may have a direct influence on the emission of cluster ions from those elements with different isotopes though its mechanism is not very clear.[17]

From this point of view it is easy to understand that the relative intensity of sodium cluster ions does not show alternation because sodium has only one natural isotope

^{23}Na. But the relative intensity $I_{he}(N)$ and ratio R as well as the relative yields of heteroisotopic cluster $(^{63}Cu_{N-1}\ ^{65}Cu_1)^+$ have shown alternations because copper has two natural isotopes as ^{63}Cu and ^{65}Cu in the sample. Therefore, it is certain that the isotopic effect is an important factor in the formation of polyatomic ion clusters by sputtering.

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