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Cluster Abundance Spectra of Low Melting Temperature Metals Produced by Bombardment of 6keV Xe atoms

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We have carried out the measurements of cluster abundance spectra for the low melting temperature metals In, Ga, Sn and Bi bombarded by 6keV Xe atoms. The obtained spectra show a quite different nature compared with the previously observed spectra for the 3d transition metals, i.e., the high melting temperature metals. We have observed two new types of spectra. One is expressed by a combination of an exponential function and a power function in the case of In and Ga, and the other by a combination of an exponential function and a log-normal function in the case of Sn and Bi. In both cases, the exponential function-like behavior suggests that an explosive release of monomer atoms occurs just after the bombardment and the cluster formation proceeds via monomer absorption at some later stage. A power function-like behavior in the former case may be interpreted as a cluster formation via bond-breaking on the remnant surface, while the log-normal function-like behavior is substantially new. Such behavior is rather common to a cluster formation via cluster coalescence under the course of aggregation process in high-density gaseous environment, which is unlikely to occur in the present case, i.e., a singly driven short time phenomenon.

Key words: Cluster, Sputtering, Low melting temperature metals

1.INTRODUCTION

It is well known that the flux of particles released from a solid surface under bombardment with highly energetic atoms generally contains clusters as well as atomic species. At present, concerning a projectile of sputtering event, its behavior was well represented by linear cascade theory. However, as a matter of fact, even basic mechanisms of cluster emission haven't been disclosed, as its expected complication, and the formation of these clusters during a sputtering event represents one of the fundamental questions in sputtering physics.[1]

In early works of the cluster formation during a sputtering event, two ideas were proposed. One is that the cluster is directly produced as a whole from the sputtered surface.[2][3] Another is that the cluster is produced by aggregation process of each atoms produced from the sputtered surface.[4][5] Afterward, cluster abundance spectra for Ag were described well ,by first principle calculation on the basis of molecular dynamics.[6][7] In contrast to such approach, it had been recognized that a scaling hypothesis[8][9] could be applied to the cluster formation process. In these studies, it is implicitly supposed that the cluster formation is a critical phenomenon.[10][11][12]

In our previous experiments on high melting temperature transition metals sputtered with 6keV Xe atoms, we have confirmed that the cluster abundance spectra obtained were all expressed by power functions and furthermore that the scaling hypothesis was applied well with use of a critical exponent of -2.0. In order to understand further, we made the calculations based on a percolation theory.[13][14] Assuming that the metal surface consists of mutually-bond-connected atoms and the formation of a cluster takes place when all the bonds surrounding it are broken, the resulting cluster abundance spectrum was represented well by employing a suitable value of the parameter P, i.e., the broken bond probability, for each material.

Furthermore, we have observed that the parameter P is strongly correlated with the melting temperature T_m of each material. Such a correlation was understood well with use of a physical picture based on the following assumptions;

1. Thermal diffusion along the surface.

2. Associated formation of thermally isolated area, the equilibrium temperature T_{eq} given by

$$T_{eq} = T_m(e-1) \tag{1}$$

being kept much higher than the melting temperature T_m at around the bombardment position.

3. Cluster formation within the thermally isolated area as a result of bond-breaking. The broken bond probability is represented as

$$P = P_0 \exp\left(-D^* / k_B(e-1)T_m\right), \tag{2}$$

where P_0 is a normalization constant, D^* is an effective separation energy and k_B is Boltzmann constant.

However, it seemed that the above picture is not applicable in cases of the metals such as Zn, Mn, Pb and Mg. In cases of Zn and Mg, the cluster abundance spectra were expressed well by exponential functions rather than by power functions. So far, an exponential function-like spectrum was observed characteristically in the early stage of gaseous aggregation process. In connection with such observation, it may be suggested that a huge number of monomer atoms were released by a certain kind of explosion on the surface. In cases of Pb and Mg, we could not find possible interpretations for their serious deviation from the expected correlation. [15][16][17]

In anyway, it is possible that a mechanism underlying the sputtering of low melting temperature metals is different from that of high melting temperature metals. From these viewpoints, we have recently carried out a series of experiments for the cluster formation in the sputtering of low melting temperature metals.

2.EXPERIMENTS

The experiments were performed with a FAB (Fast Atom Bombardment) ion source in conjunction with a high resolution double focusing mass analyzer (JEOL JMS-HX110). Cluster cations were sputtered from the surface of target material under bombardment with Xe neutral atoms in oblique incidence of 45° with respect to the surface normal. The low melting temperature metals Ga, In, Sn, Bi and Pb were chosen as a target material. The energy of the beam of Xe atoms could be set from 1keV to 6keV. Its intensity was about ~10mA/cm^2.

The produced cluster cation was extracted by an acceleration voltage of 10kV and led to a high resolution double focusing mass analyzer consisting of a magnetic sector and an electrostatic prism. At the exit of analyzer, it was accelerated again to energy of 20keV and led to a conversion dynode detector. The whole setup was mounted in a high vacuum chamber with a base pressure less than about 10^{-7}torr during the experiments, while the working pressure was about 5×10^{-6}torr due to the operation of Xe source.

Before measurement, sputter cleaning was performed for each sample until the contamination of impurities stuck to the sample surface was removed in the monitor screen. Finally, the mass spectrum was measured by sweeping the field magnitude of magnetic sector. The same measurement was repeated 20 times, and the abundance spectrum was obtained by integrating the accumulated mass spectra.

3. RESULTS AND DISCUSSION

3.1 Experimental Results

In the present experiment, we have carried out the measurements for the low melting temperature metals In, Ga, Sn and Bi and obtain cluster abundance spectra for each of them. On the basis of percolation model, we have tried to fit each spectrum to evaluate an adequate value of P, i.e., the broken bond probability. Surprisingly, the spectra were hardly fitted to the model calculations assuming an adequate value of P. At last, it was found that the spectra could be expressed by a combination of two functions, each of which was considered to represent a typical cluster abundance spectrum. In addition to the power function so far mentioned, two new types of functions were introduced.

One is expressed by a combination of an exponential function and a power function as follows;

$$I(n) \propto \exp(-\alpha n) + n^{-\beta} \quad (3)$$

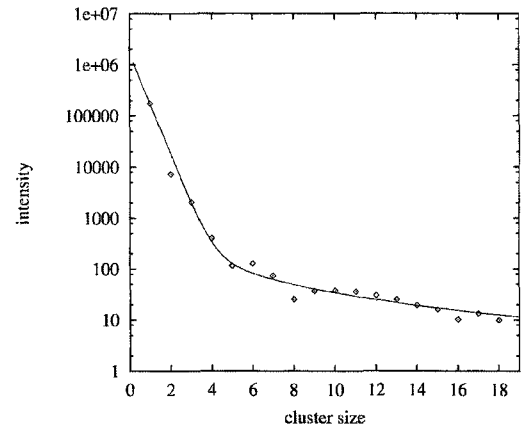

Fig. 1 Abundance spectrum of Ga clusters produced by bombardment of 6keV Xe atoms, which is represented by a combination of an exponential function and a power function (solid line).

where $I(n)$ is an abundance and n is a cluster size, in the cases of In and Ga (see Fig. 1).

The other is expressed by a combination of an exponential function and a log-normal function as follows;

$$I(n) \propto \exp(-\alpha n) + \exp(-(\ln n - \beta)^2 / \gamma) \quad (4)$$

in the cases of Sn and Bi (see Fig. 2).

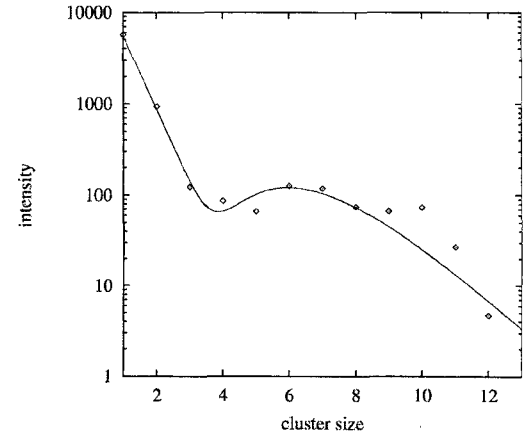

Fig. 2 Abundance spectrum of Sn clusters produced by bombardment of 6keV Xe atoms, which is represented by a combination of an exponential function and a log-normal function (solid line).

3.2 Models for Interpretation

In the cases of In and Ga, it is expected that an explosive release of monomer atoms occurs just after the bombardment and the cluster formation proceeds via monomer absorption at some later stage. More than 90 %

of secondary cations seems to originate in this process and most of thermal energy given by the bombardment of Xe atom is released as well. The exponent of power function is found to be -1.5, which should be compared with the value of -2.7 in the case of high melting temperature metal such as Cu. In other words, larger-sized clusters are produced in this case than in the case of Cu. A possible scenario is as follows;

1.An explosive monomer production takes place at first and a few monomers grow to clusters. In this case, the cluster abundance spectrum is described by the rate equation as follows;

$$dI(i,t)/dt = C_{i-1,i}(i-1,t) - C_{i,i+1}I(i,t)$$
$$I(1,0) = 1, \quad I(i,0) = 0; i \neq 1 \qquad (5)$$

where $C_{i,j}$ is a growth rate of cluster from the size i to the size j . When either $C_{i,j}$ or t is small, the resulting spectrum is expressed by an exponential function.

2.A cluster formation via bond-breaking happens on the remnant surface in succession. In this case, the cluster abundance spectrum is expressed by a power function. The temperature of remnant surface should become lower than the one in the case without such an explosive monomer production. The considerable energy is released prior to a thermal equilibrium. As a result, the broken bond probability P becomes small, comparatively.

In the cases of Sn and Bi, the observation of spectra following to log-normal functions is substantially new. Such spectra is rather common to a cluster formation via cluster coalescence under the course of aggregation process in high density gaseous environment, which is unlikely to occur in a singly driven short time phenomenon such as sputtering. If the underlying process is similar to an aggregation process, the present observation suggests an explosive release of monomer atoms with a high density core. In this case, the cluster abundance spectrum follows to the rate equation (5) but under the condition that both $C_{i,j}$ and t are not small. The resulting spectrum is a combination of an exponential function and a log-normal function. In order to understand further, the thermal conductivity of each element and the straggling of projectile Xe atom in each element may provide some hint. Both Sn and Bi are characterized by a small thermal conductivity and a deep straggling. This means that the area of monomer explosion becomes narrower and deeper in the cases of these metals compared with the cases of the metals Ga and In. As a result, it is expected that the high density core is present during explosion on the surfaces of Sn and Bi.

Figure 3 shows a correlation between a melting temperature and a variable corresponding to an evaporative latent heat, i.e., a first order coefficient in the 1/T expansion of saturated vapor pressure.[18] The cluster abundance spectra for the materials with higher melting temperature seem to be expressed by a power function, while those for the materials with smaller evaporative latent heat by an exponential function. In the lower melting temperature region, those for the materials with larger evaporative latent heat show an intermediate nature, i.e. a combination of an exponential function and some other function, i.e., a power function or a log-normal function.

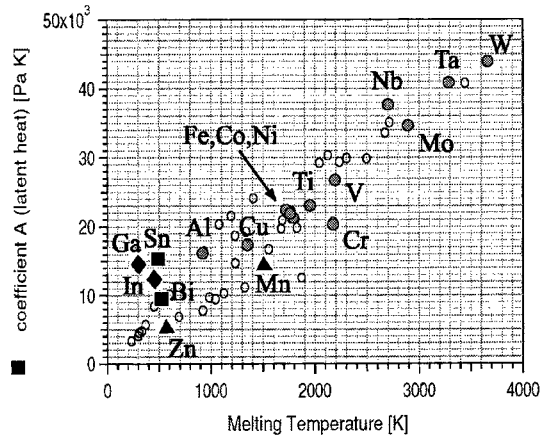

Fig. 3 Correlation between a melting temperature and a variable corresponding to an evaporative latent heat for each element, the spectrum of which is expressed by (1) power function (circles), (2) exponential function (triangles), (3) combination of an exponential function and a power function (diamonds) and (4) combination of an exponential function and a log-normal function (squares).

3.3 Effects of Target Temperature and Projectile Energy

So far, we have thought that such specific features in cluster abundance spectra mainly come from an explosive release of monomer atoms around the surface. In order to confirm this picture further, we have observed the change of abundance spectrum for In under changing the target temperature and the projectile energy.

Figure 4 shows the abundance spectra measured under changing the target temperature. In the figure, the effect of target temperature is not observed at all. This fact is interpreted in the following way. At first, as for the explosive release of monomer atoms, the energies of participant atoms are too high to be affected by tiny thermal energies obtained at the initial target temperature. Secondly, as for the cluster formation via bond-breaking, the remnant surface after explosion should be kept at low temperature because of the small remnant energy so that the broken bond probability P is kept at around the critical value, i.e., the percolation threshold 0.6. When a value of P is near the percolation threshold, it is known by calculation that the small change of the value P caused by the initial target temperature hardly affects the cluster abundance spectrum.

Figure 5 shows the abundance spectra measured under changing the projectile energy. As shown in the figure, it is found that the fraction of larger clusters tends to decrease with decreasing the projectile energy. Especially, the effect is more enhanced at lower projectile energies.

For further quantitative understanding, we have fitted the spectra to the following function;

$$I(n) = a\exp(-\alpha n) + bn^{-\beta} \quad (6)$$

As a result, it was found that the parameter α does not depend on the projectile energy. This means that the projectile energy does not affect the density of monomer atoms participating the explosion at the first stage. As for the parameter β, it was found that β tends to decrease with increasing projectile energy. This means that the increase of projectile energy leads to the decrease of the temperature of remnant surface. The ratio a/b, i.e., a ratio of the exponential function part to the power function part, shows a tendency of becoming larger when the projectile energy becomes larger. Such a tendency may be interpreted as an increase of explosive area due to larger energy deposit.

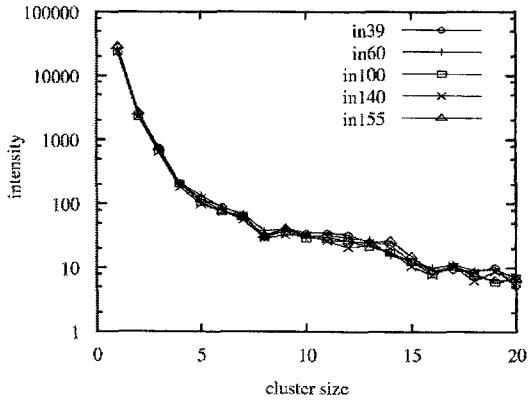

Fig.4 Abundance spectra for In measured under changing the target temperature from the room temperature to the nearly melting temperature.

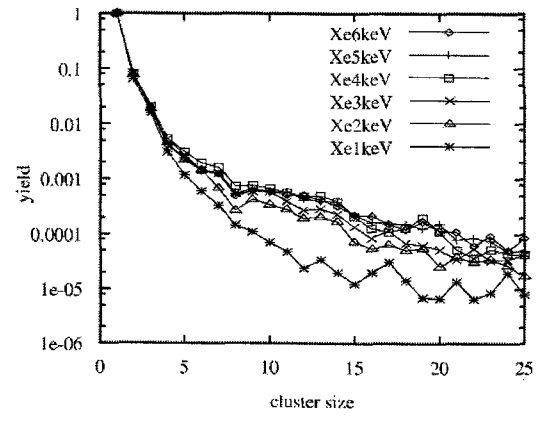

Fig.5 Abundance spectra for In measured under changing the projectile energy from 1keV to 6keV.

4.CONCLUSION

In conclusion, we have carried out the measurements of cluster abundance spectra for the low melting temperature metals In, Ga, Sn and Bi bombarded by 6keV Xe atoms. The obtained spectra show a quite different nature compared with the previously observed spectra for the 3d transition metals, i.e., the high melting temperature metals. As a result, we have identified two new types of spectra. One is a combination of an exponential function and a power function in the case of In and Ga, and the other a combination of an exponential function and a log-normal function in the case of Sn and Bi. The exponential function-like behavior suggests the occurrence of an explosive release of monomer atoms just after the bombardment followed by a cluster formation via monomer absorption. A power function-like behavior may be interpreted as a cluster formation via bond-breaking on the remnant surface, while the log-normal function-like behavior is substantially new. Such behavior is rather common to a cluster formation via cluster coalescence under the course of aggregation process in high-density gaseous environment, which is unlikely to occur in the present case, i.e., a singly driven short time phenomenon. However, if it is the case, an occurrence of an explosive release of monomer atoms with a high density core is strongly suggested. For further understanding, we have also measured the abundance spectra for In under changing the target temperature and the projectile energy. The effect of target temperature is not observed at all, while the effect of projectile energy is clearly observed. These facts seem to support the above mentioned physical picture.

REFERENCES

[1] W.O. Hofer, in *Sputtering by Particle Bombardment* thirds.:R. Behrisch and K. Wittmaack, Topics in Appl. Phys., 64, Springer-Verlag, Belrin,1991(chapter2)74.
[2] G. Staudenmaier, Radiat. Eff., 13(1972)87.
[3] W.O. Hofer, Nucl. Instrum. Methods, 170(1980)275.
[4] F. Honda et al., J. Chem. Phys., 69(1978)4931.
[5] R.A. Haring et al., Nucl. Instrum. Methods Phys. Res., B28(1987)205.
[6] A. Wocher et al., J. Chem. Phys., 105(1996)5999.
[7] S.F Belykh et al., Nucl. Instrum. Methods Phys. Res., B155(1993)409.
[8] M.E. Fisher, Rep. Prog. Phys., 30(1967)616.
[9] K. Binder, Ann. Phys. (N.Y.), 98(1976)390.
[10]M. Zinke-Allmang et al., Phys. Rev. Lett., 68(1992)2353.
[11]J.G. Amer et al., Phys. Rev., B50(1994)8781.
[12]H.E. Stanley, Rev. Mod. Phys., 71(1999)S358.
[13]M.B. Isichenko, Rev. Mod. Phys., 64(1992)961.
[14]D. Stauffer, *Introduction to Percolation Theory*, Taylor and Francis, London, 1994.
[15]I. Arai, Desorption 2000 Int. Conf., Saint Melo, France, 3-7(2000), invited talk.
[16]I. Arai, et al., Trans. Material Research Society of Japan, 26(2001)1139.
[17]I. Arai, et al., Trans. Material Research Society of Japan, 27(2002)193.
[18]C. Kittel, *Introduction to Solid State Physics*.

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