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Abundance Spectra of Clusters for Various Metals in Sputtering and Their Formation Mechanism

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We have measured abundance spectra of cluster cations for various metals produced by the bombardment of 6keV Xe atoms. Applying a scaling *Ansatz*, we have found that all the spectra overlap each other. Such a regularity suggests a cluster formation mechanism common to those metals. In this connection, we have examined a bond-breaking model assuming a mechanical break-up of sputtered surface. The model has successfully reproduced each spectrum by adjusting the parameter p, *i.e.*, a concentration of broken bonds. p has been found strongly correlated with a melting temperature of bulk material. To understand further, we have built up a more detailed model as follows;(1)thermal diffusion on the surface, (2)associated formation of thermally isolated small area, the equilibrium temperature being kept much higher than the melting point at around the bombardment position, and (3)cluster formation within the thermally isolated area as a result of bond-breaking. The model seems to work well accounting for such a strong correlation.
Key words: Cluster, Sputtering, Formation Mechanism

1. INTRODUCTION

The sputtering, i.e., the particle emission from the surface of bulk material bombarded by an energetic atomic particle, has long been studied. However, most of the published works on the sputtering have focused mainly on the measurement of the total sputtering yield while the study of the phenomenon such as cluster emission remains as one of the least understood field. Even the basic mechanism of the cluster formation has not been established yet [1].

In the earlier stage of study, the cluster formation in the sputtering was perceived as the emission of a whole particle from the bulk surface of bombarded material [2] [3]. Subsequently, the statistical agglomeration processes of individual sputtered atoms was perceived as an alternative [4] [5]. Later,*first principles* calculations of cluster emission based on molecular dynamics(MD) simulation have been carried out [6]. It was found that the MD simulation in combination with a new many-body potentials among target atoms successfully described the formation of Ag clusters in sputtering of metallic surface. Very recently, a more simplified model inspired by the results of MD simulation was proposed [7]. By considering a metal as a system of harmonic oscillators, the model successfully described the emission of large clusters in sputtering of metals Al, Nb, Ag and Ta with atomic and polyatomic ion bombardments. It was concluded that the larger clusters are emitted as whole agglomerates during the early stages of collision cascade.

It should be noted that a completely different approach to this issue emerged from a related field of research for supported clusters in parallel with the progress of such *first principles* calculations. Recent studies of the cluster formation on bulk surface with a molecular beam epitaxy [8] [9] [10] have successfully applied the scaling *Ansatz* [11] [12] [13] for the analysis and understanding of a fundamental cluster formation mechanism. They have proved the usefulness of a scaling concept and strongly suggest that the application of scaling *Ansatz* should be also useful for the study of cluster formation in the sputtering. Indeed, they have shown an alternative way to describe the cluster formation, i.e., to describe it in terms of *critical phenomena* [14]. It is greatly expected that we can get a new insight on the cluster formation in the sputtering from this new point of view.

As for the experimental observation of cluster formation in the sputtering, a power law nature of cluster abundance spectra has long been discussed in many literatures(see, for instance, [4] [15] [16] [6]). In the reference [15], it has been remarked that the abundance spectra of Cu, Ag and Au cluster ions produced by the bombardment of Cu, Ag, and Au targets with $10keV\ Xe$ ions [17] [18] can be fitted very well with a power law $N(s) \sim s^{-2.7}$ up to the highest mass s of 40. At the same time, it has been also suggested that this observation may be a signature of *critical phenomena* related to the universality classes belonging to fragmentation phenomena which concern a wide diversity of objects in nature.

Very recently, the abundance spectra of fragments produced by high energy nuclear collision has been reproduced remarkably well within a framework of a parameter free percolation model treating a nucleus as a simple fluid and it has been suggested that the per-

colation could be an universal mechanism to explain the fragmentation of simple fluid [19]. It has been also remarked that experiments with atomic clusters would help to confirm the hypothesis. In this connection, the cluster formation in the sputtering could be considered as a fragmentation of the solid surface bombarded with energetic atoms and a new systematic measurement and a new analysis along the above direction should be done urgently.

In our previous experiment, we measured the abundance spectra for 3d transition metal clusters produced by the bombardment of $6keV\ Xe$ atoms [20]. We successfully applied the scaling *Ansatz* for the cluster abundance spectra in the sputtering of 3-d transition metals for the first time and observed a striking similarity among the scaled spectra. To understand further, we carried out a model calculation based on a 2-dimensional bond percolation model with the concentration of broken bonds p as an only parameter. The model worked quite well. Furthermore, a strong anti-correlation between the concentration of broken bonds and the thermal conductivity at 976K for each bombarded material was found [21].

In the present experiment, we have examined cluster abundance spectra for various metals with diverse melting temperatures ranging from $500K$ to $4000K$. Our previous experiment has strongly suggested that the physical process of cluster formation in sputtering is closely related to the series of thermal transport phenomena, e.g., the injection of heat by $6keV\ Xe$ atom bombardment, the diffusion of heat around the metal surface, the associated structural changes in the surface, and the resulting cluster emission. We have considered that the melting temperature is a key issue making a serious effect on such structural changes.

2. EXPERIMENTAL RESULTS

We have observed cluster abundance spectra for various metals by bombarding a target material with a $6keV\ Xe$ atom coming from a FAB source(see Figure 1). The cluster cations accelerated by an extraction potential of 10 kV were guided to a high resolution mass analyzer(JEOL $JMS-HX110$) with a mass resolution of $\frac{m}{\Delta m} \sim 5000$ and a mass range up to 5000 amu.

We have applied a scaling *Ansatz* [13] for those spectra. The abundance spectrum $N(s)$ for the cluster size s should be given by a scaling form

$$N(s) = N_0 s^{-\tau} f(s/S), \tag{1}$$

where N_0 is a normalization factor, τ is a critical exponent, $f(s/S)$ is a cutoff function and S is a mean cluster size, i.e., only one characteristic size, defined by

$$S = \frac{\sum_{s=1}^{\infty} s^2 N(s)}{\sum_{s=1}^{\infty} sN(s)}. \tag{2}$$

In the equation (1), the term $s^{-\tau}$ describes a scale-independent part while the term $f(s/S)$ describes a scale-dependent one, i.e., a finite-size effect.

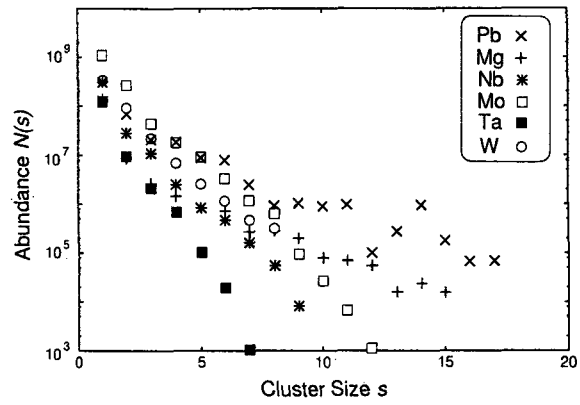

FIG. 1. Cluster abundance spectra for various materials

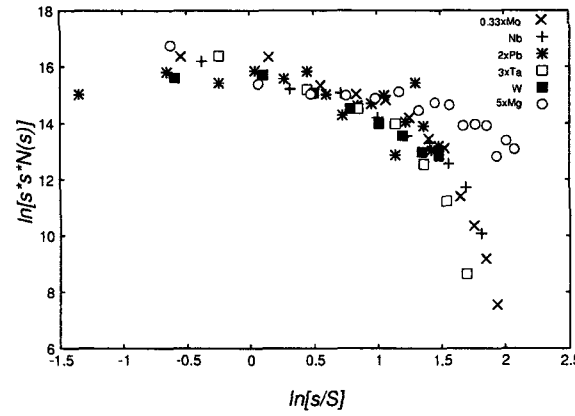

FIG. 2. A scaling plot of abundance spectra for various metals

We have made scaling plots for the measured cluster abundance spectra $N(s)$ with a value of 2, i.e., *a superuniversal value*, for τ(see Figure 2). Surprisingly, it is found that all the spectra overlap each other by adjusting their normalization factors. As a result, we have found a remarkable regularity among the measured cluster abundance spectra.

3. ANALYSIS BASED ON BOND BREAKING MODEL

To understand further, we have carried out a calculation based on a percolation theory [22] [23]. To keep the situation as simple as possible, it is assumed that the metal surface consists of the atoms arranged in 2-dimension and connected with each other by a bond and that a cluster is formed when all of its circumferential bonds are broken. Here, it should be noted that the concentration of broken bonds p is an only parameter to fit the experimental data.

Each of the measured cluster abundance spectra has been reproduced very well with a suitable value of p(see Figure 3). We assume that the bonds are broken by a thermal excitation so that the value of p for each target material should depend on both the effective

bond energy and local temperature of bombarded surface at the stage of cluster formation, which are considered closely related to the melting temperature T_m [24] and thermal conductivity k [25] of a bulk material, respectively. We have examined possible correlations between the concentration of broken bonds p and each of the T_m and k for all target materials. As shown in Figure 4, it is found that the p is strongly correlated with the T_m. As for k, any meaningful correlation has not been observed.

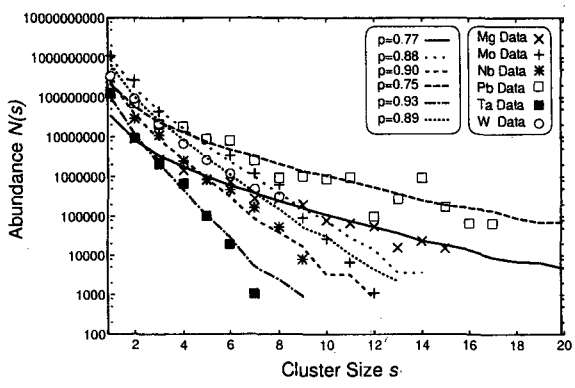

FIG. 3. Size distributions of clusters for various metals; calculations based on bond breaking model(lines) and experimental data(symbols)

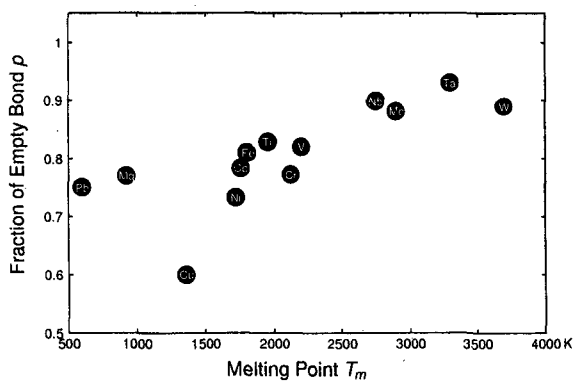

FIG. 4. A strong correlation between the melting temperature T_m and the concentration of broken bonds p for various metals;previous experimental results are included

4. PHYSICAL PROCESS OF CLUSTER FORMATION

To understand such a strong correlation, we have considered a substantially new model of the physical process underlying the cluster formation in sputtering. Our idea consists of the followings;(1)thermal diffusion on the surface, (2)the associated formation of thermally isolated small area, the equilibrium temperature being kept much higher than the melting temperature at around the bombardment position, and (3)cluster formation within the thermally isolated area as a result of bond breaking.

At first, a δ-function like temperature distribution is formed around the bombardment position. Secondly, the thermal energy is transported following the diffusion equation $\frac{\partial T}{\partial t} = \kappa \nabla^2 T$. The diffusion coefficient is given by the formula $\kappa = \frac{k}{C_\rho \rho}$ where C_ρ and ρ are the specific heat and density of target metal, respectively. At a certain time in a course of the thermal diffusion, a mechanical stress takes place around the peripheral circular area where the temperature goes down to under the melting temperature T_m for the first time shortly after going up above the T_m. As a result, the inner part bounded by the area becomes thermally isolated due to a structural discontinuity such as a flaw or a crack caused by the stress. Finally, the isolated part is kept in the equilibrium temperature T_{eq}, which is greater than the T_m, and clusters are formed by bond breaking.

At the time t, the temperature distribution $\phi(x, y, t)$ on the surface is given by the equation

$$\phi(x, y, t) = \frac{\phi_0}{2\pi\kappa t} \exp\left(-\frac{x^2 + y^2}{2\kappa t}\right), \tag{3}$$

where ϕ_0 is a normalization constant which depends on the initial condition. The bombardment point is chosen as an origin of the coordinate system. If we assume $\phi(x, y, t) = T_m$, the corresponding radius $r = \sqrt{x^2 + y^2}$ is reduced as

$$r^2 = 2\kappa t \ln\left(\frac{\phi_0}{2\pi\kappa T_m t}\right). \tag{4}$$

Then, the position of discontinuity r_{iso} is evaluated as a maximum of r as follows;

$$r_{iso} = \frac{\phi_0}{\pi e T_m} \tag{5}$$

while the corresponding time t_{iso} is given by

$$t_{iso} = \frac{\phi_0}{2\pi\kappa e T_m}. \tag{6}$$

The inner part surrounded by the discontinuity becomes thermally isolated resulting in the equilibrium temperature

$$\begin{aligned} T_{eq} &= \frac{1}{\pi r_{iso}^2} \int_0^{r_{iso}} \phi(x, y, t_{iso}) dx dy \\ &= T_m(e - 1). \end{aligned} \tag{7}$$

According to a statistical theory, the concentration of broken bonds p is a function of T_{eq} given by the equation

$$\begin{aligned} p &= P_0 \exp(-\frac{D^*}{4k_B T_{eq}}) \\ &= P_0 \exp(-\frac{D^*}{4sk_B(e-1)T_m}), \end{aligned} \tag{8}$$

where P_0, D^*, and k_B are a normalization factor, an effective dissociation energy of bond, and a Boltzmann constant, respectively. In Figure 5, it is found that the equation (8) is hold well for various metals while

Mg and Pb seem not to follow the equation. Here, we assume that P_0 and D^* are constant for simplicity. In the case of Mg and Pb, the dissociation energy D^* is expected to be considerably small compared to the case of other metals because of their small cohesive energies [24]. In addition, their melting temperatures are very low. The smaller D^* gives the larger p. This tendency is quite enhanced in the region of such low melting temperature, where the p given by the equation (8) becomes less than 0.5.

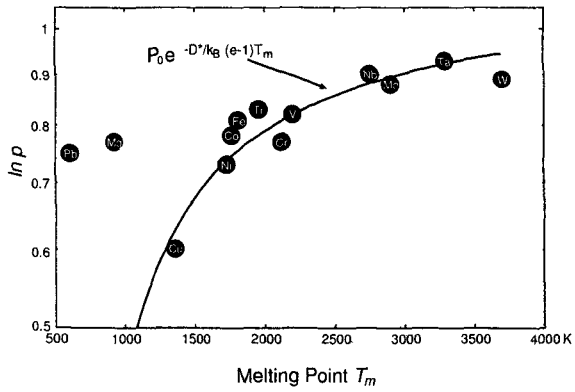

FIG. 5. A correlation between the melting temperature T_m and the concentration of broken bonds p for various metals; a model calculation (solid line) and experimental results(symbols)

5. SUMMARY

In summary, we have measured the abundance spectra of clusters for various metals produced by the bombardment of $6keV$ Xe atoms. Applying a scaling *Ansatz* for those spectra, we have found that all the spectra coincide with each other. Guided by the observation of this remarkable regularity, a bond breaking model, i.e., a variant of bond percolation model assuming a mechanical break-up of the sputtered surface, has been examined. The model has successfully reproduced all the spectra resulting in an effective value for the concentration of broken bonds p of each material. The p's are strongly correlated with the melting temperatures of bulk materials. To understand such strong correlation, we have proposed a substantially new model of the physical process underlying the cluster formation in sputtering. Our idea consists of the followings; (1)thermal diffusion on the surface, (2)the associated formation of thermally isolated small area, the equilibrium temperature being kept much higher than the melting temperature at around the bombardment position, and (3)cluster formation within the thermally isolated area as a result of bond breaking. The model has reproduced the effective value for the concentration of broken bonds p of each material very well.

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