

Critical Size of Metal Cluster in a Metal Cluster Source Controlled with a Magnetron

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A sequential growth of metal cluster from monomer is observed in a metal cluster source controlled with a magnetron. A controlled size ranging from a dimer up to several hundred of atoms per cluster is possible by an adjustment of an aggregation length, vapor pressure of carrier gas and sputter rate of magnetron. From the initial stage of cluster growth, an abrupt decrease of monomer concentration is observed which leads to the limitation of monomer absorption model. This is the first observation on the metal cluster growth from monomer as well as the existence of critical size .

Key words : critical size, metal cluster source and magnetron

1. INTRODUCTION

Nucleation from the vapor phase is usually thought to involve a stepwise clustering process in which a vapor monomer combines with a certain size cluster. When the density of clusters is high enough for coalescence, it is believed that gradually coagulation is dominant[1]. However, these two different growth processes of cluster growing show definitely different characteristic size distribution. Namely, the monomer absorption model predicted by classical nucleation theory displays a roughly exponential decreasing size distribution[2]. On the other hand, the growth of cluster by coalescence leads to a Gaussian distribution for the logarithm of the cluster size(LNDF)[3,4].

Unfortunately, neither experimental attempt has elucidated the variation of size distribution nor theoretical study has reported on a quantitative change in the size distributions in the transition from successive monomer absorption to cluster coagulation. Furthermore, nozzle expansion has been a widespread tool to study the formation mechanism for several decades. Much of the interest was devoted to calculating the critical supersaturation at the condensation onset, mean cluster size and nucleation rate[5].

In this work, we report on the first observation of the successive metal cluster growth

from monomer vapor to several hundred of atoms per cluster for the transition metals(Ti, Zr, Ta and W). Especially, the observed critical size of each metal cluster can not be described with classical nucleation theory[6]. Furthermore, we discuss the limitation of the monomer absorption model on the process of cluster growth in a cluster source controlled with a magnetron[7].

2. EXPERIMENT

As shown in the Fig. 1, metal cluster beam source consists of 2-inch planar type magnetron, aggregation tube(diameter of 100 mm) cooled down by liquid nitrogen and exit slit. Gas pressure and flow speed in the aggregation tube are controlled by the adjustment of exit slit diameter and flow rate of carrier gas(Ar, He) with mass flow controller(MFC). The argon flows directly over the target, while the helium is introduced from the back. All chambers are pumped by 500 ℓ /s grade turbomolecular pump individually.

It is well known that metal cluster can be formed through an inert gas aggregation. Especially, magnetron sputtering is preferable to control a sufficient vapor pressure in contrast to laser or Joule heating [8].

Sputtered atoms by magnetron have kinetic

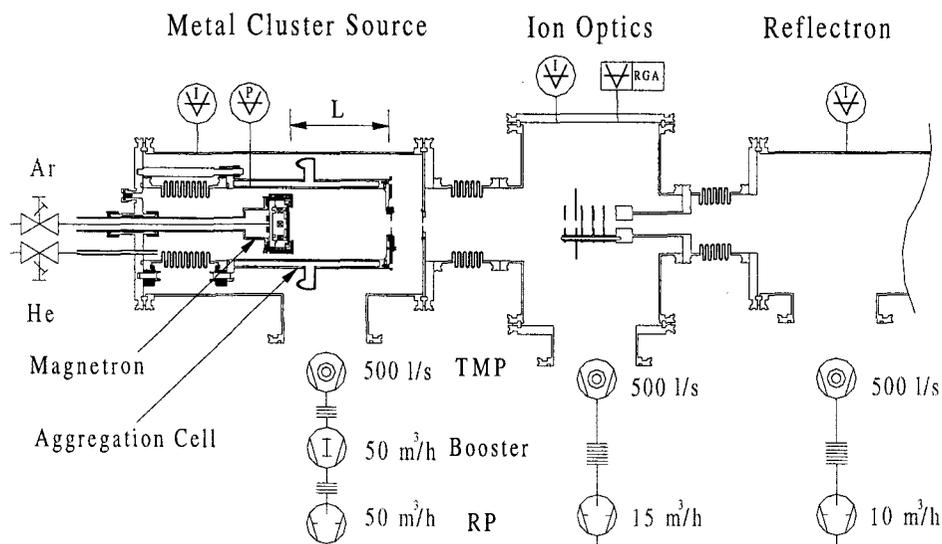


Fig. 1. Schematics of metal cluster beam source. Ion optics pulses and accelerates the positive cluster ion to reflectron for a measurement of mass spectrum.

energy which peak at a half of binding energy of target material[9] are thermalized and cooled down by collision with Ar gas in aggregation cell. Undercooling of the metal vapors brings on a supersaturation of metal vapor. At last, agglomeration of the supersaturated metal vapors results in cluster generation.

For a given gas pressure, sputter rate and gas temperature in the aggregation cell, the cluster size can be varied by changing the aggregation length(L) which is the distance between magnetron target and exit slit. Since clusters produced by this type of cluster source contain positive or negative cluster ions and neutral clusters, additional ionization process is not necessary[10]. The size distributions of clusters were measured by the reflective time of flight(TOF) spectrometer of which composed of a reflectron, a Mo conversion dynode with microchannel plate(MCP) and several ion optics for the extraction of positive cluster ions. Conversion dynode has the same structure of "Even cup"[11].

Fig. 2 shows the growth of cluster from monomer with increasing the aggregation length(L) at a given condition. Larger clusters were gradually observed with increasing the aggregation length, however, the size distribution has two dominant bands. One is ranging from 2 to 15 and the other above 15 atoms per cluster. Moreover, we observed that the position of boundary between two bands on

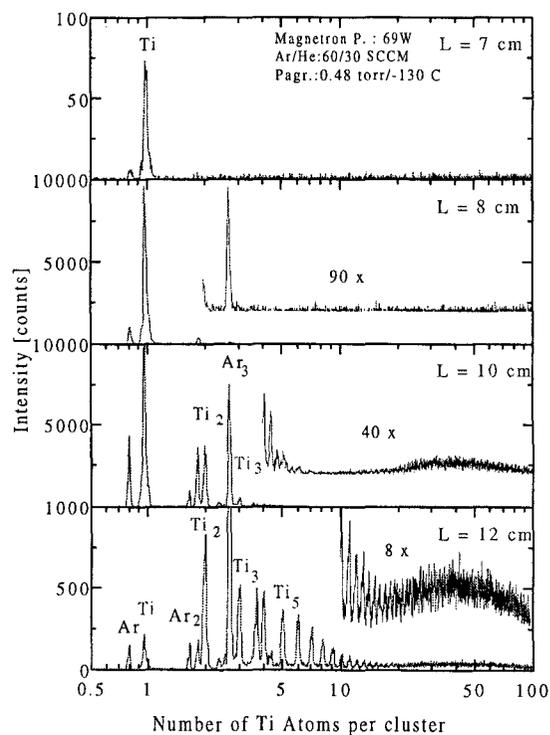


Fig. 2. Successive Ti clusters spectra related to the aggregation length. Gas pressure in aggregation tube is 0.48 Torr, magnetron power 69W and carrier gas flow rates are 60 and 30 SCCM for Ar and He respectively.

the size distribution was independent on the temperature of aggregation cell and vapor pressure of Ti.

To survey the dependence on the materials of clusters, we observed successive growth from monomer to clusters for several transition metals. All materials displayed two separated size distribution at the initial stage of growth such as Ti. However, each material has its own size of cluster at the boundary between two bands of size distribution. Fig. 3 displays mass spectra of several metal clusters. The operation pressures are individually optimized for target material in the range of 0.4~1.2 Torr with a mixture of argon and helium. The typical discharge current of a magnetron is 0.1~0.5 A at 200 V around.

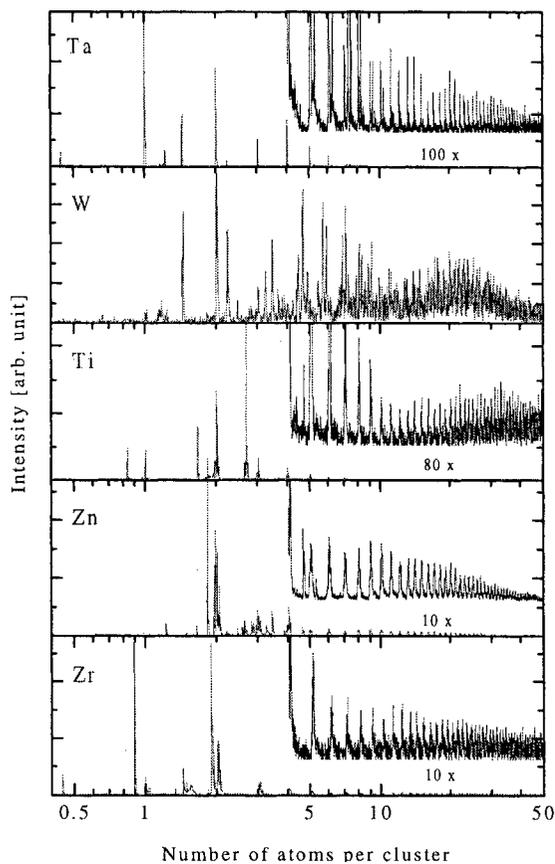


Fig. 3. Mass spectra of several kinds of clusters at the initial stage of growth. Positions of boundary between two bands on the size distribution are shown, 15 for Ti, 16 for Ta, 15 for W, 10 for Zr and 7 for Zn, respectively.

3. RESULTS

Up to now, classical nucleation theory can be widely used to explain the cluster formation on the initial stage of growth[6]. The theory gives a good qualitative description of cluster

formation. From the change of Gibbs free energy on the process of clustering, the critical size of cluster can be evaluated with

$$n_{critical} = \left\{ \frac{8 \pi r_{ws}^2 \gamma}{3 k_B T \ln P_v / P_s} \right\}^3 \quad (1)$$

where, r_{ws} is the wigner-seitz radius and γ is surface tension. P_v and P_s are the vapor pressure and saturation vapor pressure of material, respectively. Clusters with a smaller radius than $n_{critical}$ evaporate, larger ones grow. Therefore, the size at the boundary between two bands on the size distribution can be considered as the critical size of cluster.

Critical size is strictly dependent on the temperature and saturation vapor pressure. Assuming that the condensation heat can be removed by collisions with carrier gas atoms in an aggregation cell, we could evaluate critical size with Eq. 1. For Ti, the calculated critical size is smaller than the size of a monomer, since $\gamma=1,650$ dyn/cm, $P_s(500\text{ K}) \sim 10^{-35}$ Pa, $P_v \sim 10^{-5}$ Pa and atomic radius(1.35 Å). The typical ion temperature of the glow discharge plasma has been used. Neglecting the loss of the sputtered atoms by the carrier gas, P_v can be estimated by the products of discharge current(0.35 A), sputtering rate of Ti(0.88 for 200 eV Ar ion) and considering the drift velocity of carrier gas in an aggregation cell($v_{drift} \sim 30$ cm/sec).

Unfortunately, our experimental results were enormously deviated from the classical nucleation theory. The critical size of Ti cluster was observed around 15 atoms/cluster.

To observe the temperature dependency of critical size, the temperature of aggregation cell

material	γ [dyn/cm]	critical size [atoms/cluster]	$E_{cohesive}$ [eV]
Ti	1650	~15	4.85
Zn	782	~7	1.35
Zr	1480	~10	6.25
Ta	2150	~16	8.1
W	2500	~15	8.9

Table 1. Derived critical sizes for various materials. Surface tension and cohesive energy in the literature are also shown.

was adjusted by the flow-rate of liquid nitrogen ranges from 173 K to 300 K. However, the variation on the position of boundary could not be observed.

Table 1. shows critical sizes of clusters for several materials observed by our experiments. Critical size can be dependent on the cluster material but not on the temperature of carrier gas.

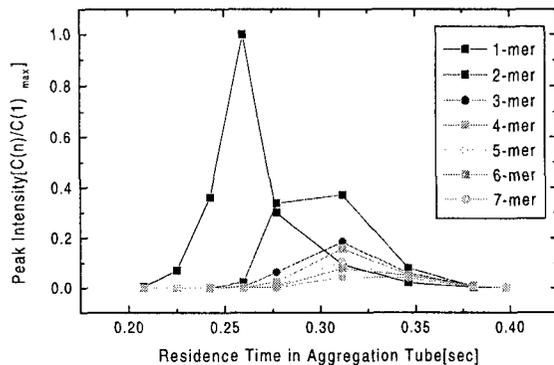


Fig. 4. Variation of intensity for each size cluster of Ti relates to residence time (L/v_{drift}) in aggregation cell.

Furthermore, from the initial stage of cluster growth, abrupt decrease of monomer was observed. Monomer sputtered by magnetron has initial kinetic energy[9]. Therefore, enough distance or gas pressure is necessary to thermalize it. Below 6 cm of aggregation length, none of peaks was observed.

As shown in Fig. 4, monomer peak intensity exponentially increases but decreases immediately due to cluster formation. As soon as clustering starts, monomer intensity become less than dimer one. This leads that the monomer absorption model can be restricted to the description for the growth of small size cluster.

References

- [1] J. M. Soler, N. Garcia, O. Echt, K. Sattler and E. Recknagel, Phys. Rev. Lett., 49, 1857-60 (1982)
- [2] T. A. Milne and F. T. Greene, J. Chem. Phys., 47, 4095 (1967)
- [3] M. V. Smoluchowsky, Z. Phys. Chem., 92, 129-68 (1917)
- [4] C. G. Granqvist and R. A. Buhrman, J. Appl. Phys., 47, 2200-19 (1976)

- [5] W. Knauer, J. Appl. Phys. 62, 841-51 (1987)
- [6] J. Frenkel, "Kinetic theory of liquids", Oxford University press(1946) pp. 366-426
- [7] T. Hihara and K. Sumiyama, J. Appl. Phys. 84, 5270-5276 (1998)
- [8] M. Ohring, "The materials science of thin films", Academic Press Inc. (1992) pp 132-133
- [9] K. Meyer I. K. Schuller and C. M. Falco, J. Appl. Phys., 52, 5803-05 (1981)
- [10] H. Haberland, M. Mall, M. Moseler, Y. Qiang, T. Reiners and Y. Thurner, J. Vac. Sci. and Tech. A, 12, 2925-30 (1994)
- [11] D. Bahat, O. Chesnovsky, U. C. Even, N. Larie and Y. Magen, J. Phys. Chem., 91,2460-62 (1987)

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