

Melting of small silver clusters investigated by HT-GIXRD

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Keywords: cluster, phase transformation

Abstract. Silver clusters of different size have been produced by magnetron sputtering in a gas aggregation nanocluster source and deposited on silicon wafers. The cluster size (9 – 20 nm) was influenced by varying the aggregation tube length. X-ray reflectometry measurements show very small overall film densities and thus reveal the deposition of separate clusters.

The samples were investigated by means of grazing incidence X-ray diffractometry (GIXRD). Lattice constants were determined from centre of gravity of the Ag(111) reflections. The cluster sizes were calculated from the Fourier coefficients of the physical line profile. It is found that the lattice constant slightly increases with increasing cluster size for clusters up to 12 nm, but decreases for larger cluster sizes. Nevertheless the measured lattice constants of the deposited silver clusters suggest a residual tensile strain for all samples. This observation seems to be in discrepancy with the expectation of smaller lattice constants, i.e. a compressive strain, because of increasing influence of the surface energy for small particles. Following the GIBBS-THOMSON theory, the melting temperature should decrease with decreasing particle size. Melting points significantly lower than the bulk value were found by High-Temperature GIXRD for all samples. The measured melting temperatures are in good agreement with the theoretical values, what confirms the calculated cluster sizes.

Introduction

The physics and chemistry of nanoscale systems have advanced significantly over the last 10 years and there are attractive prospects for translating the original scientific developments into a new generation of high technology materials and processes [1,2].

Clusters are aggregates of atoms or molecules, generally intermediate in size between individual atoms and aggregates large enough to be called bulk matter.

Researchers in material physics and statistical physics try to understand the collective behavior of matter from the entropy, temperature, young modulus or dislocation. Other fields such as atomic and molecular physics or chemistry concentrate on the behavior and interaction between single atoms and molecules. Although a bulk material is composed by individual atoms or molecules the study lines of the above mentioned fields seem to be incompatible with each other. At this point the particles in the intermediate range between atoms and bulk matter called clusters and more precisely cluster physics can give answers.

For small and medium sized clusters a large fraction of the component particles are located on the surface. So there is a strong link between the chemistry and physics of clusters and that of the surfaces of bulk matter.

Here we report on the influence of cluster sizes on lattice parameters and cluster melting points. Cluster size selection was carried out by varying the cluster forming chamber (aggregation tube) length.

Experimental

Figure 1 shows the schematic sketch of the experimental set-up, which is equipped with a NC 200 nanocluster source (Oxford Applied Research) inside a vacuum chamber. The experimental setup has two main regions. The first part is called *sputtering and cluster forming chamber* followed by the *deposition chamber*.

Argon was used as sputtering gas. The target (2" Ag) atoms are sputtered out by a direct current (dc) magnetron based on a concept developed by Haberland et al. [3-5]. Clusters form by the attachment of free atoms and coagulation processes [6] inside the liquid nitrogen ($1-N_2$, 77 K) cooled aggregation tube of variable length. Inside the liquid nitrogen cooled aggregation tube argon cools and sweeps the atoms and clusters from the aggregation region towards a variable exit diaphragm. Clusters were deposited on Si(100) substrates placed within the deposition chamber.

The tube length was varied between 8 and 16 cm. The longer the tube, i.e. the longer the time the particles need to pass through aggregation tube, the larger the cluster size should be because of increasing number of collisions.

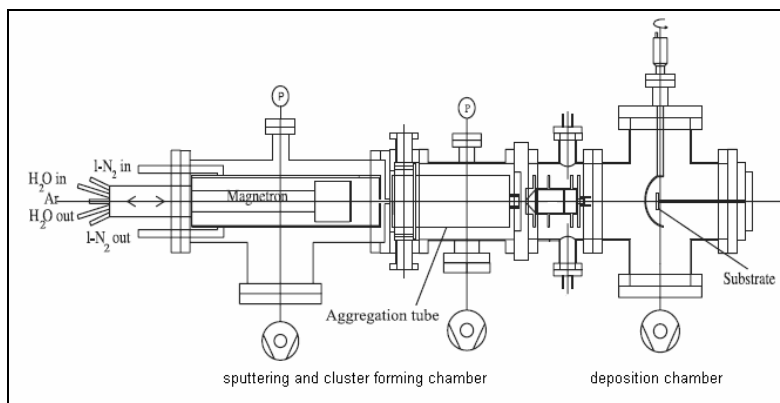


Figure 1 Schematic view of the experimental set-up

All samples were investigated by grazing incidence X-ray diffractometry (GIXRD). The measurements were carried out on a Θ - Θ -diffractometer XRD3000 (Seifert) with a special thin film attachment. Cu-K α radiation (40 kV, 40 mA) was used with an incident angle of $1.0^\circ/2\Theta$. The cluster sizes as well as lattice constants were determined from the Ag(111) reflection by means of the fitting program WINFIT1.2 [7].

Experimental determination of the cluster melting point was done in situ by measuring the Ag(111) reflection at elevated temperatures using the Bühler HDK2.4 mounted on the XRD3000. The pressure within the chamber was $5 \cdot 10^{-3}$ mbar. For each measurement the sample was heated up to a certain temperature with a heating rate of 10 K/min. The holding time before starting the measurement was 30 min to guarantee full temperature equalization within the chamber. Measurements were carried out in steps of 100 K and 20 K near the expected melting point, respectively. Since the silver fcc lattice is destroyed due to melting, the silver diffraction peak will disappear. The temperature at which no Ag(111) reflection could be observed was taken as melting temperature for the specified cluster size.

Results and discussion

Determination of cluster size and lattice constant

The cluster size was determined from the X-ray diffraction line profile of the Ag(111) reflection using a simplified variant of Warren-Averbach method under the assumption that no microstrain broadening occurs [7].

The experimental line profile is composed of several components. The profile related to the sample is broadened by convolution with the instrumental profile. The instrumental profile was determined by measuring LaB₆ standard material (SRM660 [8]) and removed by Fourier-Stokes method [9, 10]. The remaining sample profile was Fourier transformed and the coefficients were plotted versus the harmonic number. The steepest part of this plot is linearly extrapolated to 0, which gives the mean number of coherently diffracting domains representing the cluster size [7].

Figure 2 shows the mean cluster size depending on the aggregation tube length. As expected, the mean cluster size increases with increasing tube length. Because of the longer residence time of the clusters inside the aggregation chamber the number of collisions within the aggregation chamber increases, resulting in larger clusters.

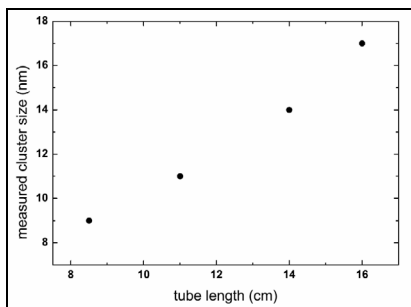


Figure 2 Cluster size depending on aggregation tube length

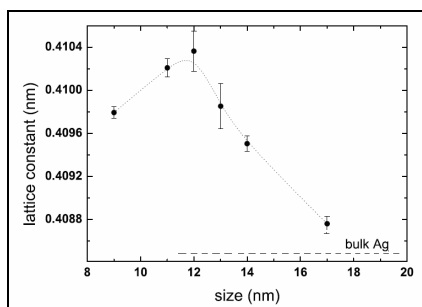


Figure 3 Lattice constant depending on cluster size

The lattice constant calculated from the centre of gravity of the Ag(111) reflection is shown in figure 3. With reference to direction of strain measured we found a tensile strain within the clusters for all samples. The lattice constant is increasing for cluster sizes up to 12 nm. For larger cluster sizes it converges to bulk value. Concerning a constant amount of silver atoms deposited, one should expect some kind of compressive strain for small cluster sizes, because of the increasing influence of surface energy. However, the size effect of nanoparticles on the lattice constant is described in many articles and the authors found decreasing as well as increasing lattice constants with size [11–14]. It seems that the size effect on the lattice constants strongly depends on the deposition conditions (particle-surface interaction) and the nanostructure evolution during cluster growth (inter-particle interaction). This point will be investigated and discussed in detail in future work.

Investigation of melting behaviour

The melting point of bulk silver is 1233 K.

Figure 4 gives an example of in situ high temperature GIXRD measurements. The peak shift to lower 2θ angles is caused by thermal expansion of the silver clusters. The temperature at which the Ag(111) reflection disappears was taken as the melting temperature for the sample. No crystalline silver was found after cooling down the sample. This fact can be ascribed to an evaporation process of the molten silver clusters at the low pressure within the HDK2.4 high temperature chamber.

We found melting points between 770 K and 925 K for our samples (dots in figure 5). This is appreciable different from the bulk value.

Theoretical considerations about the size effect on the melting point suggest a depression of melting point for the measured cluster sizes, as observed in our experiments. Since the surface is larger in comparison to the volume, small particles show some interesting properties compared to bulk material. Apart from increased vapour pressure of small liquid droplets (*GIBBS-THOMSON effect*) [15]

$$\ln \frac{p_r}{p_\infty} = \frac{2\sigma \cdot M}{RT \cdot r \cdot \rho} , \quad (1)$$

one also observes a decreased melting point of very small particles. In thermodynamics the *CLAUSIUS-CLAPEYRON* relation is a way of characterizing the phase transition between two states of pure matter, such as solid and liquid:

$$RT \cdot \ln \frac{p_r}{p_\infty} = \frac{\Delta H(T_r - T_m)}{T_m} . \quad (2)$$

In equation (1) and (2) r is the particle radius, M the molecular weight. R represents ideal gas constant, T means absolute temperature, σ is the surface energy and ρ gives mass density. p_∞ means saturation vapour pressure and p_r the vapour pressure of small particle. T_m represents the bulk melting point, T_r the melting point of small particle and ΔH the melting enthalpy. Using equation (1) and (2) one can calculate the decrease in melting temperature ΔT for particles with radius r :

$$\Delta T = \frac{2\sigma \cdot M \cdot T_m}{\Delta H \cdot r \cdot \rho} . \quad (3)$$

The dotted line in figure 5 represents the result of equation (3).

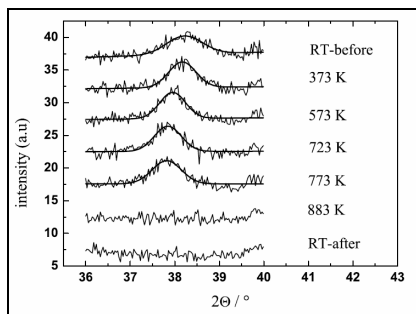


Figure 4 in-situ high temperature GIXRD measurements of Ag(111) reflection

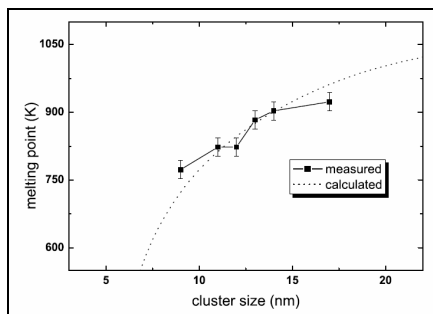


Figure 5 experimental (■) and theoretical (line) determined melting points

There is a good agreement between the experimentally determined melting points and the theoretically calculated values. This observation confirms the cluster sizes determined from the X-ray diffraction profiles.

Concluding remarks

Silver clusters of different size were produced by variation of the aggregation tube length of the cluster source and deposited on silicon wafers. The clusters were investigated using high temperature grazing incidence X-ray diffractometry with respect to lattice constants and melting points. All clusters exhibit a tensile strain, but the dependence of lattice constant on cluster size is not understood in detail. The cluster melting points are in good agreement with theoretical considerations. This confirms the determined cluster sizes and the assumption that only marginal microstrain occurs in the clusters.

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Acknowledgements. Part of this work was supported by the International Max-Planck-Research School (IMPRS) *Bounded Plasmas*. Financial support by the Deutsche Forschungsgemeinschaft through SFB/TR 24 *Fundamentals of Complex Plasmas* is gratefully acknowledged.