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Effects of oxygen addition in reactive cluster beam deposition of tungsten by magnetron sputtering with gas aggregation

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ABSTRACT

In this work, we investigated the possibilities of tungsten and tungsten oxide nanoclusters generation by means of non-reactive and reactive magnetron sputtering with gas aggregation. It was found that in pure argon atmosphere, cluster aggregation proceeded in two regimes depending on argon pressure in the aggregation chamber. At the lower pressure, cluster generation was dominated by two-body collisions yielding larger clusters (about 5.5 nm in diameter) at lower rate. At higher pressures, cluster generation was dominated by three-body collisions yielding smaller clusters (3–4 nm in diameter) at higher rate. The small amount of oxygen admixture in the aggregation chamber had considerable influence on cluster aggregation process. At certain critical pressure, the presence of oxygen led to the raise of deposition rate and cluster size. Resulting clusters were composed mostly of tungsten trioxide. The oxygen pressure higher than critical led to the target poisoning and the decrease in the sputtering rate. Critical oxygen pressure decreased with increasing argon pressure, suggesting that cluster aggregation process was influenced by atomic oxygen species (namely, O^- ion) generated by oxygen–argon collisions in the magnetron plasma.

1. Introduction

Tungsten oxide is widely investigated for its use as the base material in different applications, such as gas sensors [1], electrochromic devices [2], photoanodes for photoelectrochemical water splitting [3] or as a catalyst in polymer electron membrane fuel cell [4]. It was found that doping of tungsten oxide with noble metals can lead to significant changes of the properties of these devices [5,6]. Studies of fundamental physical and chemical principles hidden beneath the function of these devices are often performed on well-defined epitaxial model systems. Those systems were usually composed of small metal islands on oxide surface. In recent years, systems with inverse order of materials, i.e., oxide islands on metal surface, were found to be an attractive model for investigation of role of oxides in catalytic process [7]. Such systems are often called inverse catalysts.

In this work, we examine possibilities of using magnetron sputtering with gas aggregation as a tool for production of tungsten oxide nanoclusters to be used in various tungsten oxide/metal model systems. This technique was first introduced by Haberland et al. [8], and since then, it was thoroughly investigated theoretically and experimentally (e. g. [9–12]). Clusters created by this technique were investigated for use in various applications, such as microelectronics, electronics, optics, gas sensors, catalysts, etc. [13]. Thanks to its ability to generate small mass controlled clusters to be deposited on practically any surface, it is promising technique to be used for creating tungsten oxide on metal inverse catalyst. However, it has not been investigated for the generation of tungsten or tungsten oxide cluster yet. The goal of our work is to examine the mechanism of tungsten oxide clusters generation in reactive atmosphere.

2. Experimental details

A magnetron based gas aggregation cluster deposition system designed by HVM Plasma (detailed description can be found in [14]) was used for production of tungsten and tungsten oxide clusters. It consists of three parts: cluster source, quadrupole mass spectrometer (QMS) and deposition chamber.

A 2″ planar magnetron designed to work in high pressures was used as a sputtering source. It is placed in cylindrical aggregation chamber and can be moved axially to vary distance from the exit nozzle in range 60–250 mm. Aggregation chamber has 100 mm diameter and can be cooled by water or liquid nitrogen. The exit nozzle can be changed to have diameters 2–6 mm. Argon of purity 6.0 and oxygen were admitted into the chamber via two mass flow controllers. The cluster source is ultra high vacuum compatible with ultimate pressure of 10^{-6} Pa. Quadrupole mass filter (Oxford Applied Research QMF200, described in [15]) can be used to cluster mass measurement and filtration. Deposition chamber has a carrousel for up to four samples, load

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lock system and quartz crystal monitor (QCM) for determination of the deposition rate.

For our experiments, depositions were made from pure tungsten target. Magnetron was working in a DC mode with the discharge power of 100 W. Aggregation chamber wall temperature was stabilized by flowing water and aggregation length was set to 200 mm. Exit nozzle had 4 mm diameter. The relation between pressure in the aggregation chamber (P[Pa]) and gas flow (f [sccm]) in this configuration is as follows:

$$P = -0.0017 * f^2 + 1.466 * f$$

For the determination of morphology and chemical state, clusters were deposited on Si wafers and investigated ex situ by x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM) at the Surface Science Laboratories of Charles University in Prague. For XPS measurement, we used the Specs XR50 x-ray source with Al anode and the VSW HA100 hemispherical analyzer with multi-channel detection located in the vacuum chamber with ultimate pressure under 10^{-8} Pa. Spectra analysis were performed in KolXPD software using the fitting procedure described in [16]. SEM measurements were performed on Tescan MIRA3 FEG microscope with electron beam energy 5 kV. For AFM measurements, we used Bruker MultiMode8 microscope operating in PeakForce tapping mode [17].

3. Results and discussion

In the first phase of experiments, we investigated cluster production in pure argon atmosphere. Fig. 1 shows dependence of cluster diameter and deposition rate on argon flow into the aggregation chamber. Cluster diameter was obtained by fitting cluster mass distribution obtained by QMS with lognormal distribution. An example of measured mass distribution and fitting for argon flow 30 sccm and 100 sccm can be seen in Fig. 2. Cluster diameter is obtained from mass values considering spherical clusters composed of pure tungsten. In both QMS and QCM data at Fig. 1, we can see different behaviour for lower (<40 sccm) and higher (>60 sccm) argon flows. While under 40 sccm, the increase in argon flow rate led to the slight increase in both cluster size and deposition rate, at higher flow rates, the increase led to the formation of smaller clusters and higher deposition rates. Increasing deposition rate can be explained by increasing discharge current and better focus of the cluster beam. For better understanding of the difference in behaviour for lower and higher flow rates, we have to consider two different processes that take place during cluster aggregation: three-body and two-body collisions. Cluster seeds are created by collision of two sputtered tungsten atoms and one argon atom [18]. Argon is needed in this process to carry away part of the condensation heat. Cluster seeds resulting from this process can condensate into the larger clusters via two-body collisions [19]. Independently of conditions, the probability of cluster seed formation via three-body interactions is the deciding factor for the amount of generated clusters [20,21]. At the lower argon flows, the low probability of three-body interactions results in smaller number of created clusters and therefore low deposition speed. As the amount of sputtered atoms that are not consumed in the cluster creation process is higher and material drift velocity through the aggregation region is lower at the low argon flow rates, cluster growth via two-body interactions plays a dominant role at these conditions. This results in a small number of large clusters (Fig. 1) and a broader size distribution (Fig. 2). At higher argon flows, the probability of three-body interactions raises, resulting in the higher cluster generation rate. As the number of clusters increases, cluster growth is suppressed [21]. This effect is pronounced by a shorter transit time of aggregates in the aggregation region caused by a higher material drift velocity [22]. As a result, we observed a large number of smaller clusters. Deposition rate increases and cluster size decreases with increasing argon flow (Fig. 1). Other factors that can play role in the increase of the deposition rate are increasing discharge current and better aerodynamic focus of the cluster beam. The mass distribution of clusters is narrower than that in the previous case (Fig. 2).We can say that the three-body interactions are dominant at these conditions. Similar behaviour was observed for palladium clusters [22].

In the next step of our experiments, we examined the influence of oxygen admixture on the cluster aggregation and properties at various argon flow rates. Fig. 3 shows dependence of cluster aggregation rate on amount of oxygen admixed into the working gas. Response to the

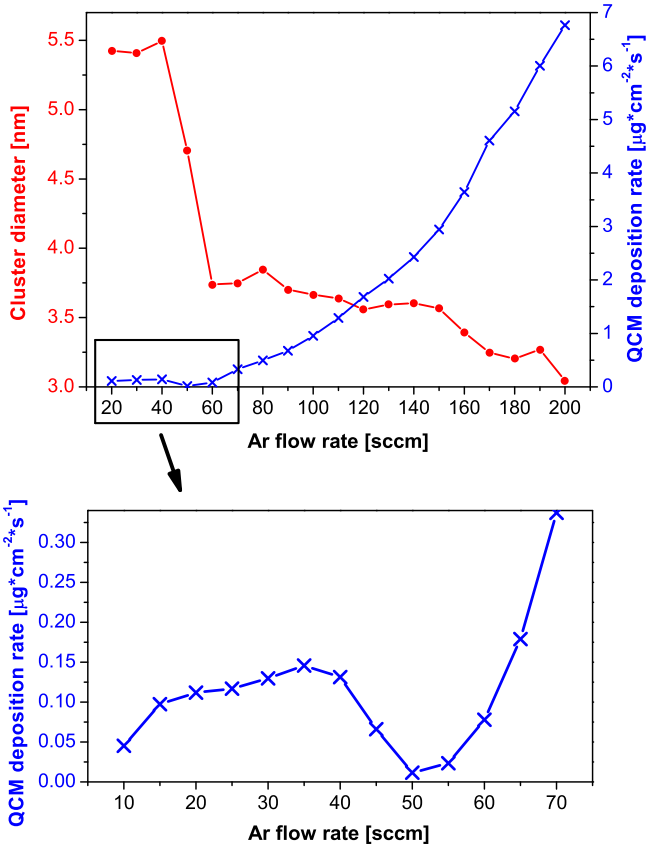

Fig. 1. Dependence of cluster diameter (left axis, dots) and deposition rate (right axis, crosses) on argon flow during sputtering and aggregation in pure argon atmosphere.

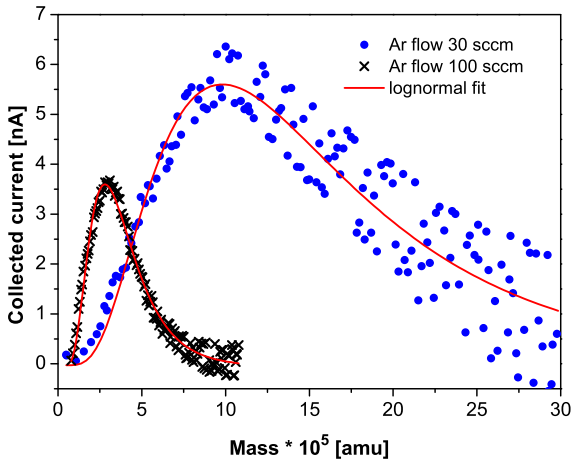

Fig. 2. Mass spectra of clusters generated in pure argon atmosphere at argon flow 30 sccm(dots) and 100 sccm (crosses).

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