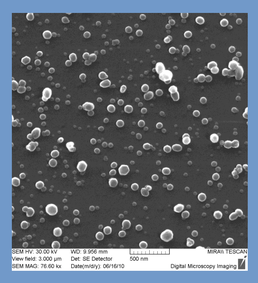
Gas aggregation nanocluster source - reactive depositions of copper and titanium nanoclusters



Aleš Marek, Jan Valter, Stanislav Kadlec, Jiří Vyskočil
HVM Plasma, spol. s r.o., Prague, Czech Republic
e-mail: Ales.Marek@hvm.cz

Introduction

Production of clusters by magnetron based gas aggregation technique [1] exhibits high degree of ionization of clusters and therefore the possibility of deposition of clusters with well-defined size (using mass filtering) and energy distribution (using substrate biasing). This technique can produce clusters with broad range of sizes – from nanometers to tens or hundreds of nanometers – in dependence on the operating conditions. Magnetron based nanocluster source enables the operation with both metallic and non-metallic materials [2, 3].

Some authors mentioned [4, 5] and we have observed [6] great importance of contaminants or background gas on the cluster seed formation. The aim of the work presented in this contribution is to study the influence of added oxygen on cluster production.

Experimental setup

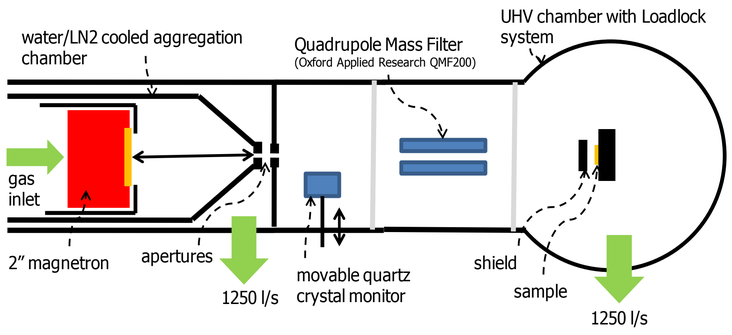


Fig. 1: Schematic of the nanocluster source used in experiments. Design HVM Plasma.

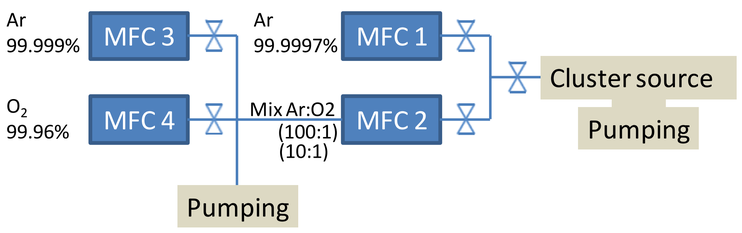


Fig. 2: Schematic of the gas mixing arrangement for fine oxygen input.

The magnetron based gas aggregation source (Fig. 1) consists of a 2" planar magnetron adapted for operation up to 300 Pa. It is immersed into a cooled aggregation chamber with variable length (60 – 250 mm) and an exchangeable exit nozzle (diameter typically 2 – 6 mm). The whole nanocluster sputtering tool is designed as UHV (ultra high vacuum) with ultimate pressure 1.10^{-6} Pa after baking out. Cluster beam can be sampled by movable quartz crystal monitor and by Quadrupole mass filter (Oxford Applied Research QMF100) that operates in mass range up to 3.10^6 a.m.u. in case of single charged clusters. Clusters can be deposited in a UHV deposition chamber equipped with a carrousel for 4 samples and a load lock system.

Gas feeding system for the fine oxygen addition into the working gas is depicted in Fig. 2. Two mass flow controllers (MFC) were used for preparing a mixture Ar:O_2 100:1 or 10:1. This "diluted" oxygen was added through the third MFC into the aggregation chamber. This enabled addition of oxygen with minimal step of 0.005 sccm.

All experiments presented in this contribution were carried out with the aggregation chamber cooled by water, with the exit nozzle 4 mm of diameter, argon working gas, copper or titanium target and magnetron operated in dc mode. Argon gas pressure of 160 Pa in the aggregation chamber corresponds to flow 124 sccm with the used nozzle. Quadrupole mass filter was used with resolution 25% in all presented measurements.

Results - Copper clusters

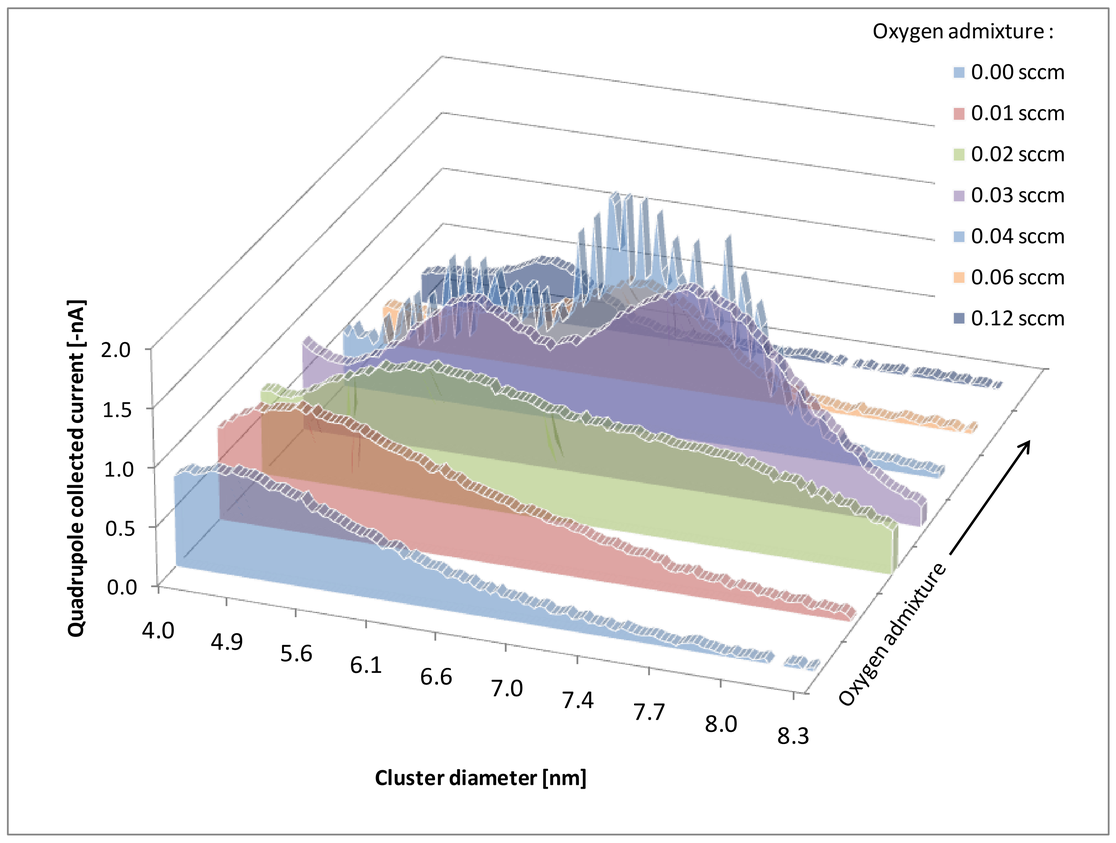


Fig. 3: Quadrupole mass spectra in cluster diameter representation – influence of oxygen admixture on the cluster production. Discharge conditions: Cu target, pressure in the aggregation chamber 160 Pa (i.e. 124 sccm of Argon flow), discharge power 100 W, aggregation length 160 mm.

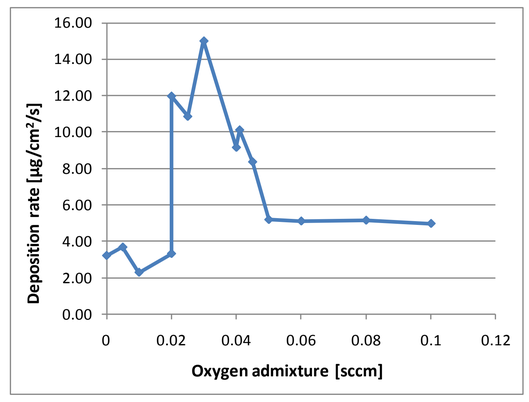


Fig. 4: Quartz Crystal Monitor data captured at the same experimental conditions as in Fig.3.

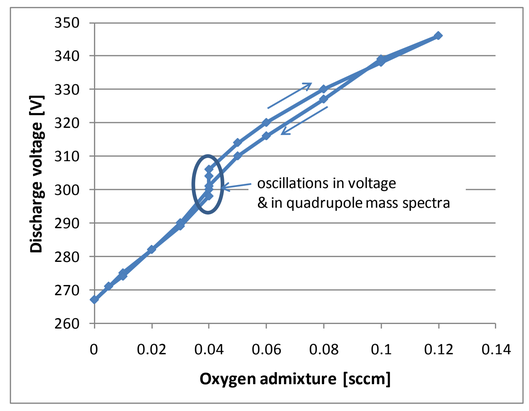


Fig. 5: Discharge voltage in dependence on the oxygen admixture. The same experiment as Fig.3

COPPER CLUSTERS

Figure 3 describes the evolution of Cu cluster mass spectra when the oxygen admixture increased from zero to 0.12 sccm. At 0.03 sccm, the cluster production reaches its maximum due to very enhanced formation of bigger clusters. This can be clearly seen in the quartz crystal measurements in Fig. 4 as a tall maximum around 0.03 sccm. Little more of O_2 (0.04 sccm) leads to an unstable state with oscillations of the mass spectrum followed by vanishing of the bigger clusters. This second transition, again, is confirmed by the deposition rate evolution. Nevertheless , the final state at 0.12 sccm is still different from the one without oxygen, namely from the point of view of the discharge voltage (Fig. 5).

So there are 3 distinct modes of the cluster production: First, the clean mode (no oxygen), second, the low oxygen mode (till 0.03 sccm O_2) and third, the high oxygen mode (0.12 sccm or more). Both the **observed transitions are reversible:** when decreasing the O_2 admixture back from 0.12 to 0 sccm, the evolution of mass spectra follows back the one observed when increasing the O_2 flow. Even the instability at 0.04 sccm was reproduced. The 0.04 sccm instability can be seen at the voltage as well. The three modes are shown schematically in Fig.10.

The deposited clusters themselves are shown on a TEM image in Fig. 6 together with the cluster size diagram obtained by TEM image analysis and with the corresponding cluster size spectrum obtained by the quadrupole mass filter. Their comparison shows good agreement what indicates good relevance of the mass spectrometry.

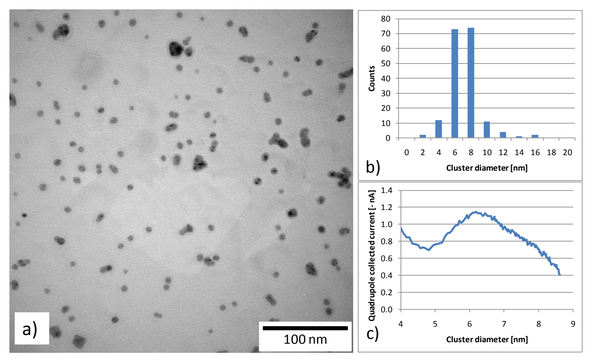


Fig. 6: a) TEM image of deposition at discharge conditions corresponding to Fig.3: Cu target, 160 Pa, 100W, 160 mm, none oxygen addition; b) histogram of deposited clusters; c) quadrupole collected current in this experiment

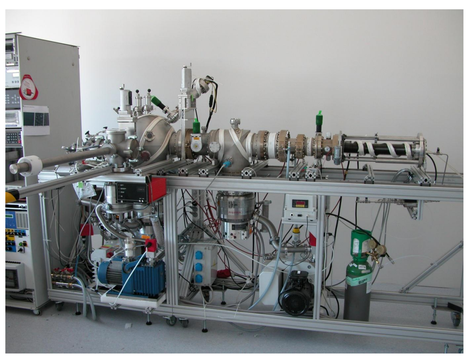


Fig. 7: Nanocluster source. HVM Plasma.

Conclusions

- Small oxygen admixture influences the cluster formation considerably
- Three distinct modes of cluster production (see Fig. 10)
- The onset of this effect is in the order of 10 ppm (Cu clusters) or 100 ppm (Ti) of O_2 in the Ar working gas
- Transitions between modes are reversible in case of Cu

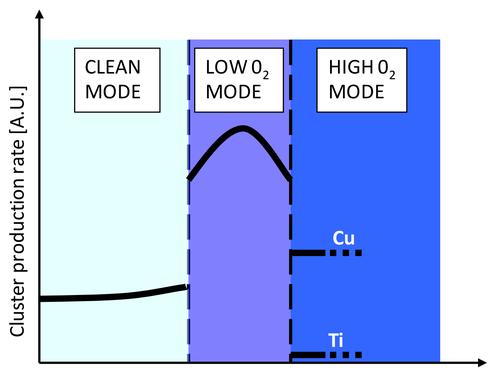


Fig. 10: Schematic summary of the cluster production rate dependence on the oxygen admixture

Titanium clusters

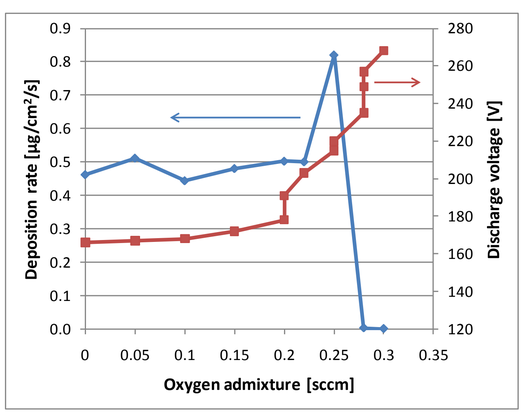


Fig. 8: Quartz crystal measurement of cluster production rate and discharge voltage in dependence on the oxygen admixture. Discharge conditions: Ti target, pressure in the aggregation chamber 160 Pa, discharge power 200 W, aggregation length 160 mm.

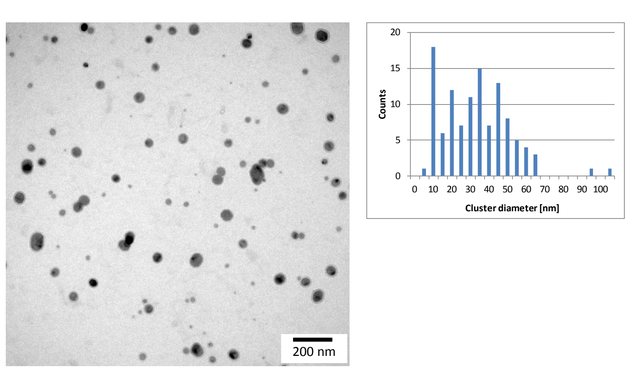


Fig. 9: TEM image and cluster size diagram of deposition at discharge conditions similar to Fig.8: Ti target, 150 Pa, 200W, 160 mm. None oxygen addition.

In case of titanium we can observe similar behavior as in the case of copper clusters. Clean mode, the low oxygen mode with enhanced cluster production and the high oxygen mode. No cluster production was observed in the high oxygen mode probably because of target poisoning. The quadrupole mass filter data are not given here, because almost all of produced clusters are bigger than the operation range of our quadrupole mass filter (13 nm in case of titanium). This fact is visible in transmission electron microscope data depicted in Fig. 9 – deposition for TEM was prepared at conditions similar to that in Fig. 8.

Acknowledgements:

This work was supported by the grant KAN101120701 of Academy of Sciences of Czech Republic. We thank for TEM analysis of our samples to Vladimír Starý, Faculty of Mechanical Engineering at Czech Technical University in Prague and Nataliya Murafa, Institute of Inorganic Chemistry of the Academy of Science, Czech Republic.

References:

[1] H. Haberland, J. Vac. Sci. Technol. A 10 (1992) 3266.
[2] A. Banerjee, Rev. Sci. Instrum. 79 (2008) 033910.
[3] S. Pratontep, Rev. Sci. Instrum. 76 (2005) 0451003.
[4] T. Hihara, J. Appl. Phys. 84 (1998) 5270.
[5] K. Wegner, J. Phys. D: Appl. Phys. 39 (2006) R439.
[6] A. Marek, ECNF 2010 conference proceedings