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SPUTTERING RATES AND NANOSCALE CLUSTER PRODUCTION IN A HOLLOW-CATHODE APPARATUS

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Abstract—*By combining a hollow-cathode plasma sputter device with the gas aggregation technique, an intense source of nanoscale metal clusters has been developed. Net sputtering rates have been measured as a function of pressure, flow velocity, electric current and cathode geometry, and in most instances they were found to behave differently than their planar-electrode sputtering counterparts. Deposition rates on substrates located away from the hot plasma region have been also measured. Clusters of Cu, Ag, Au and Ta have been produced and their size has been determined via XRD and TEM. The size of* Cu_n *clusters is found to increase with the sputter source discharge current.*

INTRODUCTION

The synthesis of materials by consolidation of clusters was first suggested in the early 1980s by Herbert Gleiter (1) and was applied initially to metals (2), and then to nanophase ceramics (3). Since then, owing to the potentially revolutionary properties of nanostructured materials, several different physical, chemical and mechanical methods have been developed and devoted to the synthesis of such materials. For a recent relevant review see Ref. (4).

In the still-growing list of methods devoted to the production of nanostructured materials, the cluster beam deposition technique will continue to hold a prominent place because, if for no other reason, this is the only convenient way to produce films with nanocrystalline structure composed of size selected clusters. The same technique, furthermore, allows to study cluster substrate interactions and finally to vary the energy of the deposition, leading to important technological applications (5).

A first necessary step for the synthesis of clusters in the gas phase is the vaporization of materials. Among the physical methods (resistive evaporation (2), laser evaporation (6) and sputtering (7)) used for that purpose, sputter deposition is the most versatile technique, since, in principle, any material can be sputtered in good yield.

A practical problem with the plasma sputter technique, however, has to do with the conflicting requirements imposed on the pressure of the noble gas needed in the discharge. Specifically, while the efficient aggregation of the sputtered atoms into clusters demands a larger than usual inert gas pressure, this enhanced pressure may hinder the transportation of the sputtered material and the subsequently formed clusters to the substrate. Therefore, one has either to compromise with relatively low pressure for good rate of transportation but low efficiency for cluster production, or to increase the pressure, usually in the range between 300 and 700 mTorr, in order to secure efficient cluster formation and use a thermal gradient to enhance the rate of deposition (8-11). The thermal gradient itself, however, can strongly affect the properties and the structure of the deposited clusters.

The objective of the present study was to develop a convenient sputtering apparatus for the production of continuous beams of large clusters of refractory metals, in particular, utilizing an alternative approach not only for the sputtering configuration, but also for the transportation and the deposition of the clusters. Since the device was developed, among other reasons, for the fabrication of nanostructured materials in macroscopic quantities, a few additional conditions should be satisfied. The density of the cluster beam, for instance, must be as high as possible, a requirement which, it should be noted, is not needed in most other applications of clusters. Furthermore, the clusters must be transferred with good efficiency over a relatively long distance in order the deposition to take place in a clean environment as far away from the hot plasma region as possible.

These objectives were realized by combining a hollow-cathode, glow-discharge sputter source with the gas aggregation technique (12, 13). The prototype of the hollow- cathode source used here was developed at the Niels Bohr Institute of the University of Copenhagen and a brief description of it has been recently presented (14).

Presently, we describe the apparatus as it has been developed at Democritos, including the source for the production of the clusters and the two differential pumping stations for the formation of the beam of clusters, and demonstrate that this device can produce large, nanoscale size clusters. We first report, however, on the performance of the apparatus on sputtering yields and deposition rates. We consider this information worthwhile, not only because these rates are expected to have direct consequences on the formation and the properties of the clusters, but also because data associated with hollow-cathode devices, although not completely missing (15), are nevertheless very scarce in the international literature.

APPARATUS AND PRINCIPLES

Figure 1 shows an overview of the apparatus. Ar gas, at various pressures (usually at about 1 mbar) and adjustable velocities, enters into the apparatus via the hollow cathode, shown at the extreme left side in Figure 1, and then proceeds through the anode, which is at ground potential.

The sputtering device consists of a copper cooling block drilled to accept very tightly a metal insert which functions as the cathode. The cooling block has machined internal passages through which distilled water or oil can be circulated. External cooling of the cathode is, in fact, required, since typically 100-400 watts are used during an experiment.

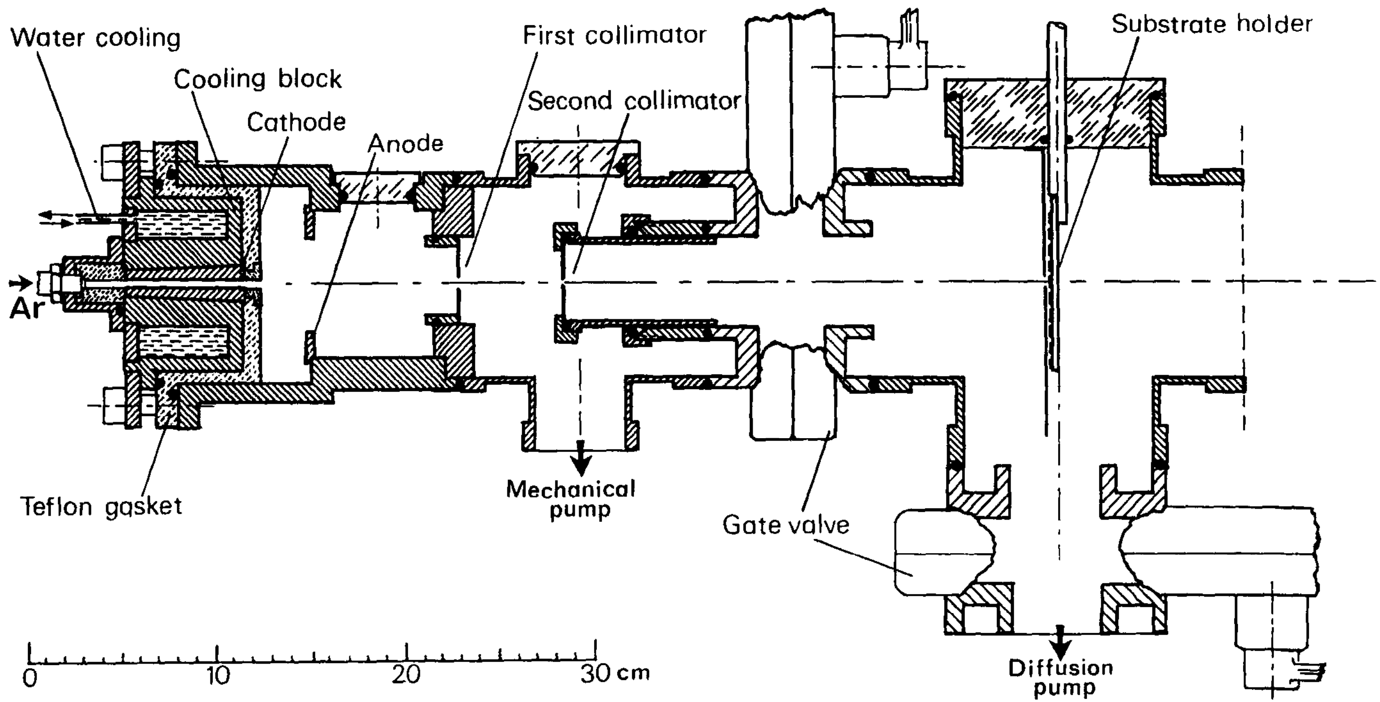

Figure 1. Apparatus and principle of the experiment. Atoms are sputtered from the inner walls of the hollow cathode under a dc plasma discharge. The discharge is operated near 1 mbar and this high pressure leads to the aggregation of atoms to clusters. The clusters are swept by the gas stream through the first collimator, fly through the second collimator and are deposited onto a substrate located in the last vacuum chamber at the extreme right.

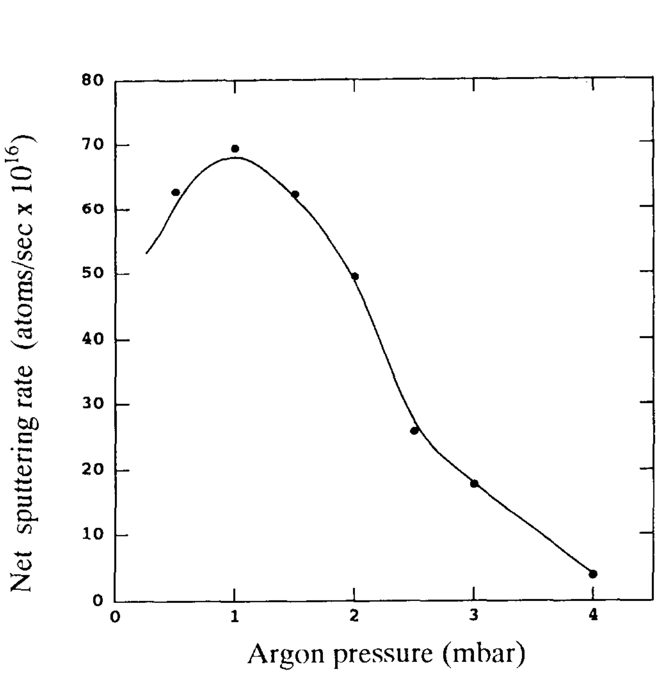

Figure 2. The net sputtering rate of Cu as a function of the Ar pressure at the exit of the hollow cathode under constant Ar throughput. The line through the points is drawn to guide the eye.

The cathode, manufactured from the desired metal, is designed to require a small amount of material. Externally, it has the geometrical shape of a cone (see Figure 1). That particular external shape was chosen because it allows a very tight fitting of the cathode within the cooling block for good thermal conductivity. The conical cathode, however, has been perforated along its long axis in the shape of a right circular cylinder, which acts on the one hand as the target in the sputtering, and on the other hand as the channel through which the gas needed in the discharge enters into the system. Various cathodes with central circular cylinders of diameter between 3 and 8 mm and length between 3 and 5 cm have been drilled and tested. For experiments with certain metals, such as Au or Pt, a rolled foil placed into the central cylinder of hollow Cu cathode was used. The cooling block with the hollow cathode is attached to the vacuum tube by means of a Teflon gasket and bolts bearing Teflon bushings, which ensure the electrical insulation of the cathode from the rest of the apparatus.

When a floating potential difference of about 340 V, driven by a dc power supply, is applied between the insulated cathode and the grounded anode (which includes the walls of the vacuum tubes), a glow discharge ionizes the noble gas. The Ar^+ ions, accelerated towards the cathode, are allowed to sputter metal from only the walls of its inner cylinder, since all other sides of the cathode or the rest of the cooling block are protected by the Teflon cover.

The number of clusters coming directly from the cathode target diminishes under the above conditions (16). The clusters are formed in the rare gas surrounding the discharge. In fact, the inert gas serves two purposes apart from maintaining the plasma. First, it slows down the sputtered atoms. Once their kinetic energy is low enough, stabilizing atomic collisions occur which can lead to the formation of clusters.

The formation of a Cu dimer can be written in presence of Ar:

$$Cu + Cu + Ar \rightarrow Cu_2 + Ar \qquad [1]$$

The dimer formation is the first necessary step in the condensation process. Nevertheless, similar equations describe the subsequent growth of the larger clusters. As noted in Eq. [1], the atom of the inert gas seems to behave merely as a spectator. However, three atoms at least are absolutely necessary in the cluster formation process; otherwise energy and momentum conservation cannot be fulfilled simultaneously. In principle, the spectator atom in Eq. [1] could as well be a third Cu atom. However, that probability is practically insignificant.

The second role of the flowing gas is to sweep the clusters away from the plasma and the condensation region, having thus significant effects on the formation of the clusters, since it practically determines the residence time of the metal vapor in the region of interaction.

Very important parameters of the system are the pressure and the flow rate of the inert gas, which need to be precisely controlled. The gas pressure is measured after the anode (see Figure 1) in the first expansion region and its typical values tested range from 0.5 to 5 mbar. However, the pressure found to be most efficient for cluster production was about 1 mbar and this is the pressure most often used. The values of the gas throughput presently tested range between 0.5 and 3.5 mbar.lit/sec at 25°C, causing a commensurate average flow velocity of the gas at the exit of the hollow cathode between approximately 15 and 120 m/sec, respectively. The clusters composed from atoms, which at the time of the sputtering are assumed to have zero flow velocities, eventually obtain equilibrium values that are similar to the flow velocity of the inert gas.

In order to maintain a steady gas flow, the Ar gas introduced through the hollow cathode is evacuated first by a mechanical pump located in the chamber between the two collimators. These collimators have variable diameter with typical values 5 mm and 1 mm for the first and the second collimator, respectively. Finally, the region following the second collimator is evacuated by a diffusion pump. The clusters are swept by the gas stream through the first collimator, fly inertly through the second collimator, and then are deposited on various substrates under high vacuum.

SPUTTERING RATES

In the utilization of a sputter source for the production of metal clusters, sputtering rates assume a decisive role because these determine whether the density of metal atoms sputtered in the gas phase will be sufficiently high to allow condensation of the metal vapors to clusters. Furthermore, it is reasonable to expect that different densities of sputtered atoms will result in clusters with different size. Therefore, the ability to understand and manipulate sputtering rates offers a means to select the optimum conditions for the production and utilization of clusters. We shall attempt below to delineate the effect of a number of parameters on sputtering rates.

In order to render the discussion of the ensuing experimental data more comprehensible, it should be first emphasized that the number of atoms initially sputtered from a cathode is almost always larger than the number of atoms permanently escaping from that cathode because the latter is the outcome of two competing processes: initial sputtering and redeposition. Obviously, only their difference, which may be referred to as the net or apparent sputtering rate associated with the number of atoms permanently escaping the cathode in unit time, can be determined experimentally. In the present study the net sputtering rate was determined from the weight lost from the cathode during a certain discharge.

The effect of inert gas pressure on the net sputtering rate of Cu is demonstrated in Figure 2 under a constant Ar throughput and constant electric current, where it may be seen that the apparent sputtering rate has a maximum at about 1 mbar and decreases either at higher or lower pressures.

It may be instructive to try to understand the above behavior. At the higher pressure region the present data are fully consistent with the corpus of relevant data available in the literature. According to that previous experience, the sputtering rate keeps decreasing with increasing pressure simply because the redeposition due to backscattering monotonously increases with increasing pressure (16).

The behavior of the sputtering rates below 1 mbar, however, is not so easily understandable, since all the previous sputtering rates available in the literature either increase with decreasing pressure or below a certain pressure assume a constant value (17). Since, however, the previous data were more or less all collected in planar-electrode configurations, the different behavior presently observed should be associated with the unique geometrical features of the hollow cathode. It is important to recognize in that respect that, in addition to redeposition due to backscattering which is present in both configurations, in the hollow cathode situation redeposition can also occur via diffusion to the walls of the inner cavity of the cathode opposite to the site of a sputtering event.

It is interesting to note that the redeposition due to backscattering and redeposition due to diffusion have opposite sign dependence on gas pressure. This can be best visualized in terms of the mean free path of the sputtered atom, which keeps increasing with decreasing gas pressure and *vice versa*. At low pressures the mean free path becomes sufficiently long for the diffusion to the opposite walls to become important. With increasing pressure, the decreasing mean free path confines the sputtered atoms closer and closer to the wall from which they have been emitted, rendering the redeposition due to backscattering more important. Accordingly, the decrease in the net sputtering rate observed in Figure 2 below and above 1 mbar seems to be associated with redeposition due to diffusion and redeposition due to backscattering, respectively.

However, in the present sputtering system operating under continuous and rather copious flow of gas, the above somewhat static explanation in terms of pressures exclusively cannot be but half of the story. A second very important parameter associated with the gas flow is, in fact, the residence time of the sputtered atoms within the narrow cavity of the cathode. One expects that as the velocity of the gas decreases, the residence time of the evaporated metal within the cathode increases, resulting in bigger redeposition by either mechanism, and thus smaller net sputtering rate. The opposite effect is expected with increasing velocities.

The importance of flow velocity is demonstrated in Figure 3, which is an alternative view of the data in Figure 2. Specifically, since the data in Figure 2 were collected at various pressures under constant throughput, each pressure corresponds to a different value of gas velocity, which can be easily estimated. The net sputtering rate data of Figure 2 are replotted in Figure 3, this time versus gas velocity. A comparison between Figures 2 and 3 shows a rather revealing association. Specifically, the very low sputtering rates seemingly caused by high pressures (Figure 2) are seen in Figure 3 to be associated with low velocities. The enhanced redeposition that causes these restricted sputtering rates, therefore, is not necessarily caused exclusively by larger pressures,

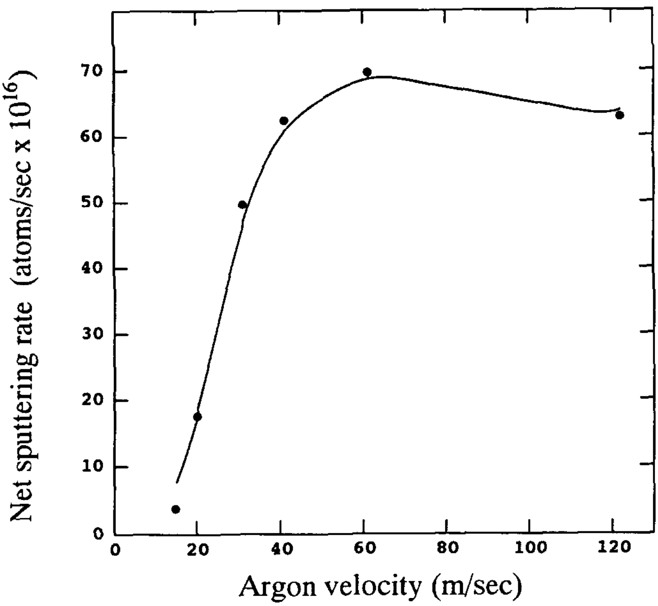

Figure 3. The net sputtering rate data of Figure 2 plotted here versus the commensurate velocity of the inert gas at the exit of the hollow cathode. The line through the points is drawn to guide the eye.

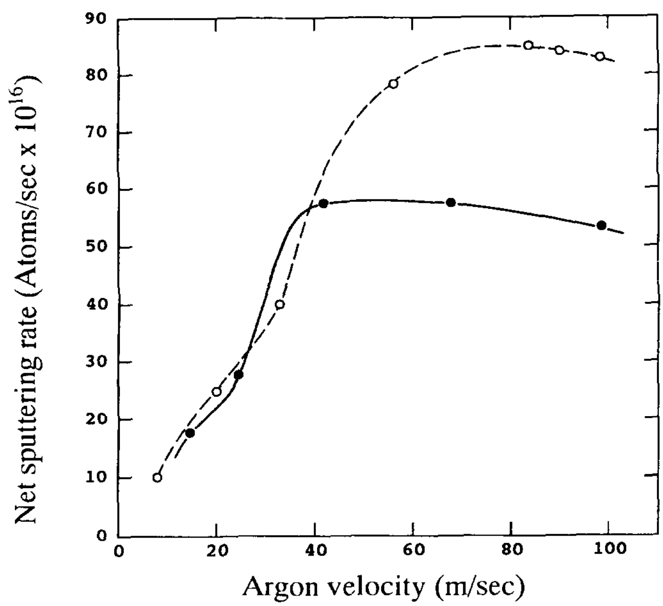

Figure 4. The net sputtering rate of Cu as a function of the Ar velocity under two pressures kept constant at the exit of the hollow cathode. The open circles correspond to 1 mbar and the closed to 2 mbar pressure. The line through the points is drawn to guide the eye.

since the same phenomenon could as well be understood in terms of smaller gas velocities, which by prolonging the residence time of the metal within the cathode, enhance its redeposition. A similar correspondence between low pressures in Figure 2 and high velocities in Figure 3 renders pressure and velocity both partially responsible for the behavior of the sputtering rates observed in the present experiment.

In order to assess individually the importance of pressure and velocity, we have measured sputtering rates as a function of flow velocity under constant pressure. Such data, demonstrated in Figure 4 for two different pressures, indicate that the net sputtering rate significantly increases with increasing velocity up to a certain value, after which it remains constant. Figure 4 demonstrates, furthermore, the effect of the gas pressure, since at 1 mbar the plateau corresponds to a significantly higher sputtering rate than at 2 mbar. The nature of the plateau and the slight decrease observed in these data at elevated gas velocities will be discussed below in the chapter on deposition rates.

Finally, Figure 5 shows the typical effect of variable electric current on the net sputtering rate of Cu under constant pressure and flow velocity, demonstrating that it increases linearly with increasing electric current. In fact no leveling off is discernible, at least within the range of the electric current values employed in the present measurements.

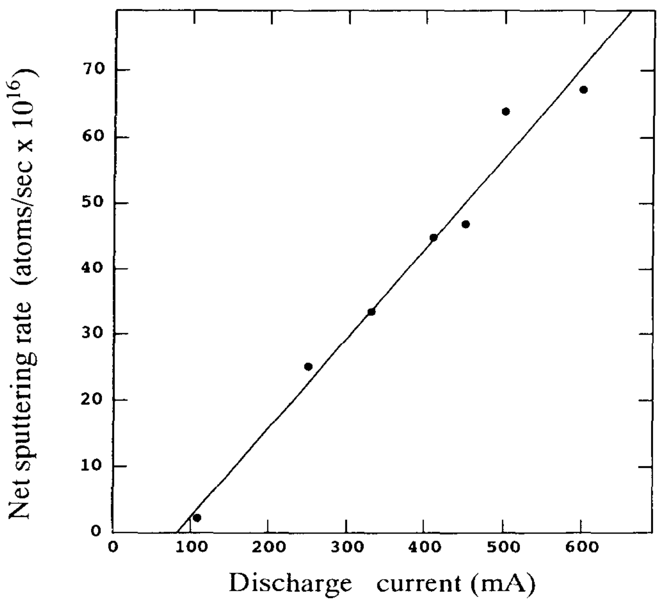

Figure 5. The net sputtering rate of Cu as a function of the electric current used in the discharge under constant Ar pressure and velocity. The line through the points represents a linear fit to the data.

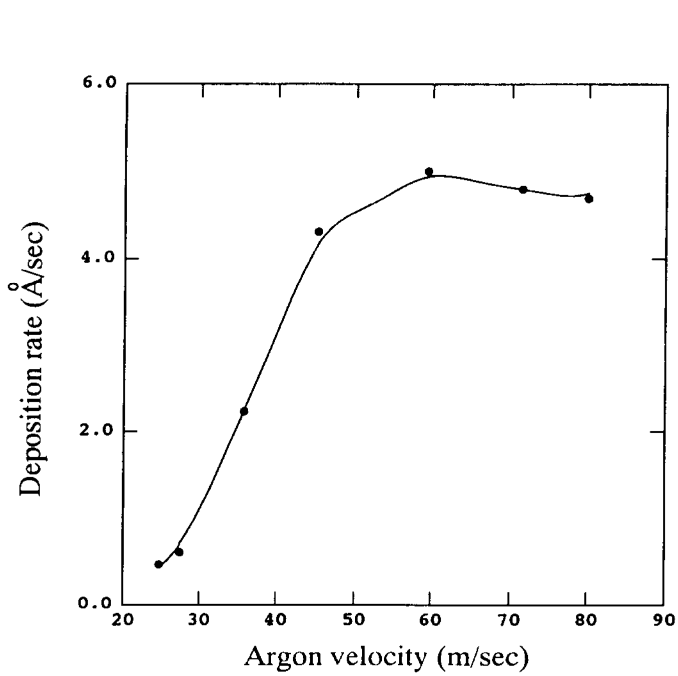

Figure 6. The deposition rate of Cu, 15 cm away from the cluster source, as a function of the velocity of the Ar gas under a constant pressure of 3 mbar at the exit of the hollow cathode. The line through the points is drawn to guide the eye.

A very important question has to do with the effect of pressure on the discharge current. If these two parameters are interdependent, then Figures 5 and 2 could be related and also explain to a certain extent the effect of electric current on cluster size (see below). For that reason, the effect of pressure on the discharge current was investigated very carefully. Although the relevant literature reports that the discharge current increases with increasing gas pressure (16), no such effect was presently observed. This difference may be explained by the different pressure domains associated with these data. It should be noted in that respect that, while the previous measurements were performed at pressures around 100 mtorr, the present measurements were performed at pressures almost an order of magnitude larger, between 0.5 and 2.5 mbar. Specifically, for a given value of an external ohmic resistance used to stabilize the operation of the source, the discharge current can by adjusted only by manipulation of the potential difference provided by the external power supply according to Ohm's law, because the potential difference between the two electrodes during the glow discharge was found to be at about 340 V, irrespective of the gas pressure.

A few more comparative tests concerning the effect of the hollow-cathode geometry on sputtering rates have been carried out. For instance, it has been found that the apparent sputtering rate of Cu does not seem to be affected by the diameter of the hollow-cathode cavity, at least when two cathode cylinders with 5-mm and 7-mm diameter holes are compared. Also, the length of the hollow cathode does not seem to affect the apparent sputtering rate, at least when two cathode cylinders 3 cm and 5 cm long are compared. Nevertheless, we believe that these results represent limited cases and that the effects of the geometrical characteristics of the hollow cathode on sputtering rates deserve further study.

It should be finally mentioned that the application of a magnetic field did not significantly increase the sputtering rates. This is consistent with the understanding (18) that the hollow cathode geometry is effectively trapping the primary electrons in the cathode dark space, which thus are permitted to expend their energy in proliferated ionization sustaining an efficient discharge.

DEPOSITION RATES

The rates with which the metal is transferred from the ion source to the substrate have, after a certain distance from the source, only marginal effects on the formation and the properties of clusters in the gas phase. Quite the opposite is true, however, as far as the cluster-substrate interaction and, thus, the destiny of the deposited clusters is concerned. In fact, the properties of thin films and presumably of nanostructured materials are affected by a multitude of deposition parameters (19), among which the rate of deposition is probably the most important (16). For that reason, we shall briefly discuss behavior of deposition rates in the present apparatus.

It should be firstly recognized that apparent sputtering rates and rates of deposition are not entirely different concepts, since in both the transfer of mass is the essential parameter. Actually, the apparent sputtering rates presented in the previous paragraphs represent nothing else but rates of deposition at zero distance from the source, *i.e.*, right at the exit of the hollow cathode.

According to the previous discussion, we expect, therefore, that the velocity of the flowing gas should be probably the most important parameter influencing the deposition rate. Thus, as it can be seen in Figure 6, at a given pressure and current, the manipulation of the gas velocity may increase the deposition rate at a point 15 cm away from the source by more than an order of magnitude, from roughly 0.3 Å/sec at low velocities to 4.5 Å/sec at higher velocities. At even higher velocities, however, the deposition rate assumes a constant value and eventually it may even slightly decrease.

An outstanding question has to do with the nature of the plateau and even more so of the decrease observed with increasing gas velocity, not only in the above deposition data, but also in the sputtering data of Figures 3 and 4. In fact, the mere presence of these features seems to contradict our whole reasoning about the importance of residence time, since according to that consideration, the sputtering and, in particular, the deposition rate could only increase with increasing gas velocity.

In order to resolve this dilemma, one has to analyze a little more carefully the particular experimental situation. It should be first reemphasized that in all the above measurements, the gas pressure is measured, controlled and kept constant at the expansion chamber following the two electrodes (see Figure 1). The constancy of the gas pressure in that region, however, does not necessarily imply that when the velocity of the gas is altered the pressure within the narrow cylinder of the hollow cathode remains also constant.

The situation within the cathode may be visualized with the help of the Poiseuille's law concerning viscous flow within a cylindrical pipe (20). The pressure P_L of the gas inside the pipe at a distance L from the exit of the pipe is given by

$$P_L = \left[P_0^2 + (16\eta L P_0 / r^2)\, v_0\right]^{1/2} , \qquad [3]$$

where P_0 and v_0 is the pressure and velocity of the gas at the exit of the cylinder, η is the coefficient of viscosity and r the radius of the cylinder.

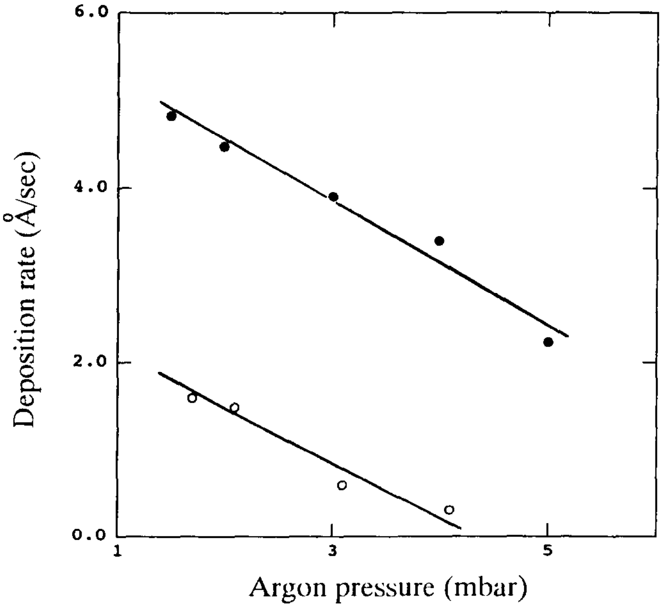

Figure 7. The deposition rate of Cu, 15 cm away from the cluster source, as a function of pressure at two different Ar throughput values. The pressure was measured after the exit of the gas from the hollow cathode. The open circles correspond to 1.5 mbar.lit/sec and the solid circles to 3.5 mbar.lit/sec. The lines through the points represent linear fits to the data.

All the parameters entering eq. [3] were kept constant during the measurements we are presently considering, except the velocity of the gas at the exit of the hollow cathode, and under these circumstances the above equation clearly indicates that the pressure at a given point inside the cylindrical cathode increases with increasing gas velocity and *vice versa*. Therefore, according to the results of Figure 2, the increasing pressure within the cathode will, after a certain point, start suppressing sputtering and consequently deposition rates. In fact, Figure 4, showing the effect of velocity on sputtering rates at two exit pressures, renders support to the above interpretation, since the deleterious effect of increasing velocity affects the sputtering data associated with the larger external pressure P_0 sooner and much more dramatically, as expected according to the above considerations and eq. [3].

Finally, the effect of directly changing the gas pressure at the first expansion chamber on the rate of deposition at two different throughputs is demonstrated in Figure 7. As expected, it is seen that with increasing pressure the deposition rate decreases significantly at both throughputs. More dramatic, however, is the effect of throughput, since for similar pressures the deposition rate increases by more than an order of magnitude by increasing the gas throughput by about 60 percent. This happens simply because under the same pressure the larger throughput corresponds to larger gas velocity.

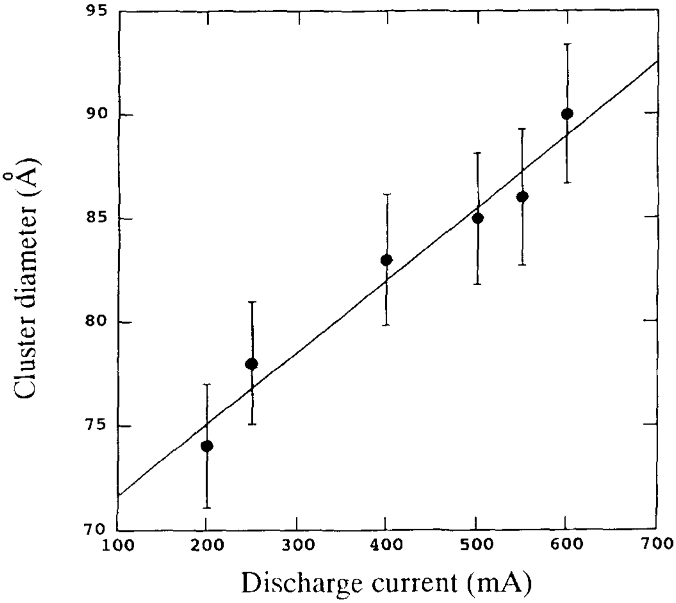

Figure 8. The mean diameter of Cu clusters deposited on glass as a function of the electric current used in the glow discharge. The line through the points represents a linear fit to the data.

CLUSTER PRODUCTION

Cluster formation in a beam is a complex process and no complete theory exists. Nevertheless, a condensation source such as that used here can be described in terms of a classical nucleation theory (21), where cluster formation is treated as a gas-fluid phase transition. Condensation normally takes a long time. Therefore, some degree of supersaturation of the metal vapor is necessary in order for the condensation to occur on the short time scale available in a beam characterized by the velocities mentioned in the previous paragraphs.

With an applied current of about 500 mA at 1 mbar pressure, a lower limit to the density of sputtered Cu of 6×10^{14} atoms/cm^3 is obtained within the hollow cavity of the cathode. At this current, the temperature close to the exit of the cathode was measured about 700 K. For these conditions the Cu vapor has a partial pressure 4×10^{-2} mbar, which is far beyond supersaturation. Thus, conditions facilitating aggregation and formation of clusters in the gas phase are present within the hollow cathode source.

In fact, we have already tested cluster production from several elements, such as Ag, Au and Ta, in addition to Cu, which is the material we have best studied thus far. In all the above tests, the average size has been determined by XRD line broadening as well as with transmission electron microscopy, which in addition gives a cluster size distribution.

We have started an investigation to identify the scaling laws of the hollow-cathode gas aggregation source; that is, the correlation between various source parameters and the size of the produced clusters. It should be noted here that scaling factors have been derived thus far only for clusters produced in supersonic sources (22), but not as yet in gas aggregation source of any kind (thermal, laser or sputter).

Some of our relevant results concerning the effect of the electric current employed in the discharge on the average size of Cu clusters are shown in Figure 8. The average cluster diameter in these measurements was determined via the X-ray line broadening technique. Figure 8 shows that an evolution of size between 72 and 93 Å can be achieved by increasing, at a given pressure and flow, the discharge current by a factor of 3. This effect of discharge current on cluster size may be understood in terms of the results shown in Figure 5, according to which the sputtering rate and, thus, the density of evaporated atoms increases with increasing discharge current. Apparently, the larger density of metal atoms in the gas phase (a condition rendering these atoms available for coagulation) favors the larger cluster size and *vice versa.*

The range of cluster size presently obtained by varying the discharge current may not be entirely satisfactory for versatile practical application of these clusters. We expect, however, to significantly extend that range when different combinations of source conditions, such as gas pressure and velocity as well as type of gas, will be systematically tested.

CONCLUSIONS

We have constructed and tested a hollow-cathode sputtering apparatus that promises high beam density and high mass distribution. The source is very easy to handle, is portable, and shows very stable running conditions. The principle allows many different materials to be exploited and is characterized by a multitude of changeable parameters to control the mass distribution, the beam density, and the deposition rate. Finally, it was found that the size of Cu_n clusters increases linearly with the sputter source discharge current.

REFERENCES

1. H. Gleiter, in *Deformation of Polycrystals: Mechanisms and Microstructures*, eds. N. Hansen, A. Horsewell, T. Leffers, H. Lilbolt, Riso Natl. Lab., Roskilde, Denmark (1981).
2. R. Birringer, H. Gleiter, H. P. Klein and P. Marquardt, Phys. Lett. A102, 365 (1984) .
3. R.W. Siegel, S. Ramasamy, H. Hahn, Z. Li, T. Lu and R. Gronsky, J. Mater. Res. 3, 1367 (1988).
4. R. Birringer and H. Gleiter, in *Clusters of Atoms and Molecules II*, ed. H. Haberland, Springer Verlag, Berlin (1994).
5. H. Haberland, M. Martin, M. Moseler, Y. Qiang, T. Reiners and Y. Thurner, J. Vac. Sci. Technol. A 12, 2925 (1994).
6. G.M. Chow, P.G. Klemens, and P.R. Strutt, J. Appl. Phys. 66, 3304 (1989).
7. H. Hahn and R.S. Averback, J. Appl. Phys. 67, 1113 (1990).
8. G.M. Chow, C.L. Chien and A.S. Edelstein, J. Mater. Res. 6, 8 (1991).
9. G.M. Chow and A.S. Edelstein, Nanostruct. Mater. 1, 107 (1992).
10. V. Haas and R. Birringer, Nanostruct. Mater. 1, 491 (1992).
11. F.H. Kaatz, G.M. Chow and A.S. Edelstein, J. Mater. Res. 8, 995 (1993).
12. F. Frank, W. Schulze, J. Urban and B. Winter, Surf. Sci. 156, 90 (1985).
13. H. Haberland, M. Karais, M. Mall, Z. Phys. D20, 413 (1991).

14. M. B. Nielsen, J. Borgrgreen, K. Hansen, J. Pedersen, B. Holst, M. Krogh, H.D. Rasmussen, E. Sondergard and A.C. Xenoulis, in *Atomic and Nuclear Clusters*, eds. G.S. Anagnostatos and W. von Oertzen, Springer-Verlag, Berlin, p. 258 (1995).
15. D.H.W. Castens, J.F. Kozlowski and D.M. Gruen, High Temp. Sci. 4, 301 (1972).
16. B. Chapman, *Glow Discharge Processes*, John Wiley & Sons, New York (1982).
17. W.D. Westwood, J. Vac. Sci. Technol. 11, 446 (1974).
18. D.G. Williams, J. Vac. Sci. Technol. 11, 374 (1974).
19. J.L. Vossen, J. Vac. Sci. Technol. 8, 512 (1971).
20. A Roth, *Vacuum Technology*, North Holland, Amsterdam (1990).
21. A.C. Zettlemoyer, *Nucleation Phenomena*, John Wiley & Sons, New York (1977).
22. O.F. Hagena, Z. Phys. D4, 291 (1987).