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Note: Proof of principle of a new type of cluster beam source with potential for scale-up

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We introduce a new type of cluster beam source based on the assembly of (metal) clusters within a condensed (rare gas) matrix. The “Matrix Assembly Cluster Source” employs an ion beam to enhance collisions between metal atoms in the matrix and to sputter out clusters to form a beam. We demonstrate the formation and deposition of gold and silver nanoclusters with mean size tunable from a few atoms to a few thousand atoms. The cluster flux is equivalent to a current nanoAmp regime but potentially scalable to milliAmps, which would open up a number of interesting experiments and applications. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4947229>]

The development of the cluster beam sources employed in many laboratories today began in the early 1980s and led, amongst other things, to the discovery of magic numbers in metal, rare gas, and carbon clusters.^{1–4} The deposition of such clusters onto surfaces represents a way to create nanostructured surfaces and materials with interesting physical, chemical, and biological properties and a range of potential applications.⁵ However the practical realisation of these applications, as well as a number of basic science experiments, is held back by the limited flux available for the current generation of cluster beam sources. In the case of mass-selected clusters of size, say, 20–2000 atoms, the cluster current available⁶ is generally limited to the nanoAmp regime, at best. If this current could be scaled up—by orders of magnitude—it might be possible to translate cluster science into a manufacturing technology. For example, in fine chemicals catalysis, if 1–10 grams of clusters could be deposited at 1% loading onto a suitable support material, one would probably produce sufficient catalyst material for the small batch production of pharmaceutical products.

In this short report, we demonstrate the feasibility of a new kind of cluster beam source—the “Matrix Assembly Cluster Source” (MACS)—based on a new principle of operation. A common method to generate clusters is by condensation of hot, vapourised (say metal) atoms in a colder gas.^{6–10} An atom of the cold gas is required, by the laws of conservation of energy and momentum, to allow the aggregation of two metal atoms in a three body collision. In the new source concept, Fig. 1, we replace the cooling gas with a cold condensed matrix, e.g., of rare gas, which represents a more efficient third body refrigerator. Left to themselves, metal atoms embedded in a cold matrix would tend to aggregate into clusters, but the rate would be limited by slow diffusion in the cold matrix. We enhance the rate of metal-metal collisions by bombarding the matrix with an ion beam. Each ion beam impact initiates a cascade

of atomic collisions¹¹ in the matrix (and no doubt electronic transitions too). To form a cluster beam, we also need to get the clusters out of the matrix and the ion beam accomplishes that by sputtering out both the metal clusters and also atoms of the host matrix. A cluster produced in the matrix environment by one collision cascade might be (i) sputtered out in the same, or a subsequent, ion beam impact or (ii) developed further by subsequent ion beam impact(s) on the matrix before being sputtered out (or the cluster might remain in the matrix or be deposited onto the matrix support). The mechanism of MACS is sputtering clusters out of a matrix, which is distinguished from direct sputtering of a (e.g., metal) target.¹²

An apparatus constructed to prove the principle of the Matrix Assembly Cluster Source is shown in Fig. 2. The metal-loaded rare gas matrix is prepared by exposing a metal grid to an overpressure of rare gas (Ar) while at the same time evaporating metal atoms (Au or Ag) into the matrix. The matrix grid used is 400 mesh (400 holes/in.) copper grid, with 37 μm square holes and 25 μm bar width, thus giving a transparency of 37%. The grid is cooled by a continuous-flow liquid helium cryostat to below 15 K, as monitored by a rhodium-iron temperature sensor in real time. The rare gas (Ar) is admitted through a precise leak valve and the dose is set by the gas pressure in the chamber monitored by a Penning gauge. Metal atoms (Au or Ag) are evaporated into the matrix, while it condenses, using a thermal evaporator. The matrix grows as an adlayer on the bars of the mesh. The metal dosing rate is monitored by a quartz crystal microbalance (QCM). The relative rates of gas condensation and metal evaporation determine the concentration of metal atoms in the matrix and thus, as we shall see, the cluster size produced. An Ar^+ ion beam with spot size of 3 mm in diameter is incident upon the matrix (perpendicular to the plane of the grid) after it is formed and clusters generated are collected by (amorphous carbon) transmission electron microscope (TEM) supports located on the opposite side of the matrix. We call this overall geometry the “transmission mode.” However, since the rare gas matrix probably condenses around the bars of the grid, rather than filling the holes completely, the

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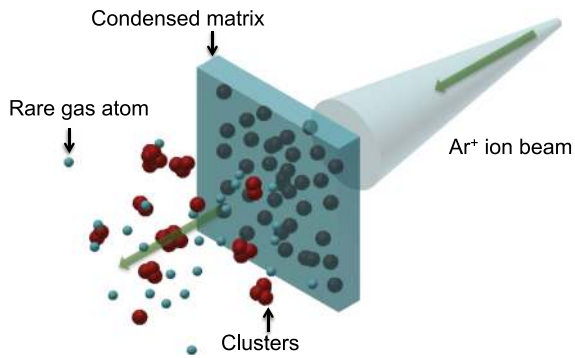


FIG. 1. Schematic diagram of the concept of the Matrix Assembly Cluster Source (MACS). The matrix is formed by evaporation of atoms of cluster material (e.g., Ag or Au) and rare gas atoms (e.g., Ar) condensed at the same time onto the matrix support grid (held at less than 15 K). Clusters are produced by high-energy Ar ions (1 keV) sputtering the matrix.

ion beam impacts which generate the clusters are more likely to be grazing events, i.e., “reflection mode” at the microscopic scale.

The images in Fig. 3, obtained from the carbon TEM supports with an aberration-corrected scanning transmission electron microscope (STEM),^{13–15} demonstrate the creation and deposition of metal clusters with the MACS. Figs. 3(a) and 3(b) are examples of STEM images of Ag clusters produced with two different matrix loading levels. The insets show atomic resolution images of individual clusters. Fig. 3(c) is a STEM image of Au clusters also generated by the MACS method. Fig. 4 is a plot of the mean Ag cluster size, obtained from the STEM cluster intensities, as a function of the metal concentration in the matrix. We observe (i) a monotonic increase in cluster size with increasing metal concentration and (ii) a size resolution of (at best) $\pm 30\%$ in the number of atoms, or 10% in diameter, noting that this is in the absence of a subsequent mass filtering stage.

Could the clusters observed in the STEM images of Fig. 3 be produced by diffusion and aggregation of metal atoms on the TEM supports themselves. This is disproved by the fact that the cluster sizes measured in sustained operation experiments

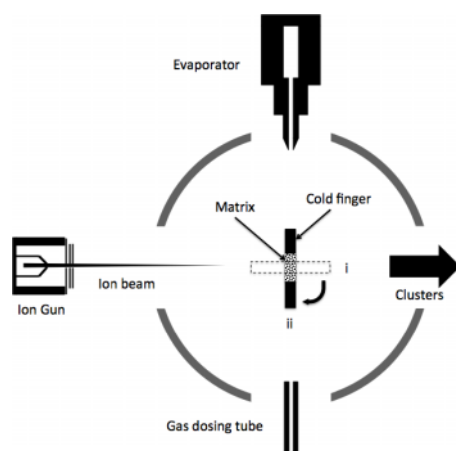


FIG. 2. Schematic diagram of the MACS apparatus. The matrix support grid is mounted on a rotatable cold finger in the centre of the chamber. The grid first faces towards the evaporator first for matrix condensation (i), then is rotated to face the ion beam for cluster production (ii).

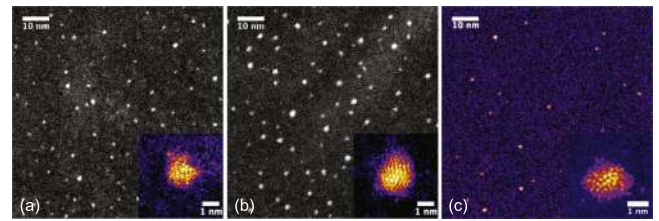


FIG. 3. ((a)-(b)) STEM images (inset at atomic resolution) of Ag clusters prepared with two different metal concentrations in the matrix, 2.3% and 3.6% respectively. (c) As (a)-(b) for Au clusters prepared with a metal concentration in the matrix of 2.3%. Related parameters: matrix support, 400 mesh copper grid; matrix temperature, 12 K, gas dosing pressure, 3×10^{-6} mbar; matrix condensation time, 200 s; matrix thickness, ~ 85 nm; Ar^+ beam current incident on matrix at 950 eV, ~ 70 nA (for Ag clusters) and 10 nA (for Au clusters); time of deposition of clusters generated from the matrix, 60 s.

are independent of the deposition time (i.e., coverage on the supports). This would not behave if clusters were formed by aggregation of atoms. The production of clusters from the matrix is also confirmed by preliminary mass spectrometer results.

An obvious question to consider is the intrinsic efficiency of the MACS. To answer this, we count the clusters imaged on the TEM supports and estimate the fraction of the incident Ar^+ ion beam flux which impinges on the holes in the grid which supports the matrix, as opposed to the bar regions of the grids. (In this estimate, we neglect those Ar^+ ions which may pass without scattering through the centres of the grid holes which we presume are unfilled.) We obtain a local efficiency of $\sim 3\%$. By efficiency we mean the number of clusters produced per argon ion incident on matrix from which a cluster beam can be formed, thus Ar ions hitting the bars are not counted. Of course the practical efficiency, i.e., area integrated efficiency, of the geometry described here is much lower, about 1%—many Ar^+ ions are “wasted” because of the limited grid transparency—but this could be addressed either by growing thin matrix

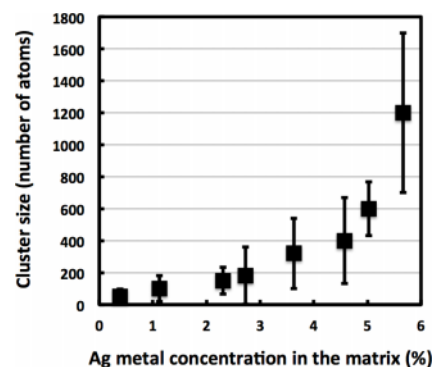


FIG. 4. Cluster size as a function of metal concentration in the matrix. The size of each cluster is measured from the integrated high angle annular dark field (HAADF) STEM intensity compared with that of single atoms. Error bars are the standard deviations of the size distributions (HAADF intensities). The circle represents the sample with the best mass resolution, $\pm 30\%$ in number of atoms, i.e., $\pm 10\%$ in diameter. Related parameters: matrix support, 400 mesh copper grid; matrix temperature, 12 K, gas dosing pressure, 3×10^{-6} mbar; matrix condensation time, 200 s; matrix thickness, ~ 85 nm; Ar^+ beam current incident on matrix at 950 eV, ~ 70 nA; and time of deposition of clusters generated from the matrix, 60 s.

films right across large voids or by operating the source in reflection mode from a matrix supported on a continuous support.

The intrinsic efficiency of the process is rather encouraging. Ion beam sources are available with currents up to about 10 A (for semiconductor processing). The efficiency estimated here implies that a cluster beam equivalent current of 0.3 A is feasible, at least in principle—a massive enhancement over presently available currents (~1 nA, as mentioned). We say “equivalent current” since the clusters produced in this demonstration may be mainly neutral in charge (if so, the problem of space charge effects in the emerging cluster beam upon scale-up will be mitigated). Such cluster beam fluxes might open up new kinds of basic measurement of clusters as well as applications of cluster materials in areas as diverse as catalysis, membranes, bio- and medical technology, photonics, magnetics, etc.^{16–21}

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