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Metallic Glasses from the Bottom-up

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Abstract

The main challenge in understanding the relation between the structure and properties of metallic glasses is describing their structure at the atomic level. Currently, their structures are considered simply *disordered* and indeed our understanding of their structure is as undefined as this term. Following the most advanced structural models of metallic glasses that are based on metal clusters, a bottom-up approach to fabrication of metallic glasses using cluster beam technology is introduced. Using metal clusters to fabricate metallic glasses from the bottom-up, that is, formation of cluster-assembled metallic glasses, provides us with the possibility of varying their structure at the atomic level while keeping their composition unchanged. A unique feature working with cluster-assembled metallic glasses is the *independent* control of their structure and composition. The advantages of this approach are presented, and its potential toward the resolution of structure–property puzzle in metallic glasses is demonstrated along with the main challenges.

Keywords: Cluster-assembled metallic glasses, metal clusters, structure–property relation, cluster deposition, cluster-based structural models

1. Introduction

First discovered in 1959 by rapidly quenching ($>10^6 \text{ K s}^{-1}$) an alloy of $\text{Au}_{75}\text{Si}_{25}$ (at.%) [1], metallic glasses (MGs) are among the most studied metallic materials. The non-periodic character of MGs underlies their unique properties which are often superior to conventional crystalline materials. Due to their reduced eddy current losses, as compared to the crystalline alloys of identical compositions, for instance, ferromagnetic MGs are commonly used as magnetic core materials [2]. Also, the corrosion resistance of iron-based metallic glasses was shown to be

much higher than that of crystalline stainless steel [3]. As another example, the $\text{Ti}_{40}\text{Cu}_{36}\text{Pd}_{14}\text{Zr}_{10}$ metallic glass is a biocompatible material that is about three times stronger than titanium, has an elastic modulus that matches that of bone, and does not produce abrasion powder [4]. Further, the combination of high toughness and high strength in Pd-based MGs puts them among the strongest and most damage-tolerant materials ever known [5].

As of now, the main challenge in investigating these materials is to describe their structure at an atomic level. In absence of an atomic description, no systematic design of MGs has been possible, and the progress in the field is merely based on the costly and inefficient procedure of trial and error. The pioneering work by Bernal [6, 7] on the structure of metallic liquids, who suggested “dense random packing of hard spheres” as the structural model, was the first step in this direction. Further research in the field has led to the discovery of many other metallic alloys that could be solidified into the amorphous state with moderate cooling rates (10^2 – 10^0 Ks⁻¹) such as $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glass for which bulk sections of 10 mm across were produced at a cooling rate of 1 Ks⁻¹ [8]. Based on the observations across the compositions of the MGs, Inoue put forward a set of empirical criteria for their formation and stability [9]. This highly valuable classification accelerated the discovery of new glass forming alloys. As a result, very soon a revision of the criteria was required [10]. Such criteria that have been proven very helpful in designing new glasses, however, naturally suffer from numerous exceptions. For instance, based on the binary phase diagram of Au–Al alloy and the relative atomic radii of gold and aluminum, it is expected to be possible to produce an $\text{Al}_x\text{Au}_{1-x}$ MG. However, to date, no one has succeeded in the production of MGs in this alloy system regardless of the employed techniques [11].

Despite the intensive research in the field of MGs, the understanding of the fundamental link between their structure and properties is still missing [12–15]. Theoretical computations have made a large contribution toward our understanding of the structure of MGs but are damned to be inaccurate due to their restricted timescale, which imposes cooling rates that are many orders of magnitude higher than what is experimentally achievable (beside the ultrafast liquid quenching reported by Mao et al. [16] with a cooling rate of $\sim 10^{15}$ Ks⁻¹). Currently, there exists no perspective to solving this issue without external help from other disciplines. Currently, the structure of MGs is addressed as *disordered* and our understanding of it is in fact as diffuse and undefined as this term. Of course, considerable progress has been made in the past toward describing the structure of MGs at the atomic level, but we are still far from having a coherent and consistent model.

Assuming we have the correct model to describe the structure of MGs, the next step would be to figure out the structure–property relation. Obviously in the absence of periodicity, it will still be much more complicated to develop this relation in MGs compared to oxide glasses considering that bond angles and lengths are much more flexible and distortable in MGs.

In this chapter, we introduce some of the most advanced experimental approaches to tackle these issues using cluster beam technology. Accordingly, this chapter aims to put forward an interdisciplinary approach and familiarize the material scientists working on MGs with cluster beam technology and how it can be used.

2. Cluster-based structural models for MGs

Although amorphous alloys lack long range order, they possess well defined nearest neighbor shells. The resulting short and medium range order is experimentally observed in MGs. The latest structural models for MGs [17–22] take this observation into account and use atomic clusters¹ to describe the structure of amorphous alloys. A structure model based on efficiently packed solute-centered atomic clusters was introduced by Miracle. In this model, atomic clusters are idealized as spherical particles, which similar to atoms, fill the space in face-centered cubic (fcc) or hexagonal close-packed (hcp) arrangements [22]. However, unlike atoms, atomic clusters can overlap and share atoms with each other. This model has gained some credit because firstly it is consistent with a broad range of previously established guidelines for metallic glasses, and secondly, it has a predictive capability for the experimentally observed medium-range order in MGs. Shortly after the presentation of Miracle's model, a revised version was suggested by Fan et al. [20] where the building blocks are again atomic clusters, but are arranged randomly instead. Later, the same group refined their model based on reverse Monte Carlo simulations and introduced the "tight-bond cluster model", which includes the clusters, the free volume between the clusters, and the interconnecting zones among clusters [19]. In a closely related approach, Dong et al. [18] introduced the "cluster-plus-glue-atom model", where the structure of the MG is described by specific metal clusters that are glued together by additional glue atoms. The recent review by Liu and Zhang [23] provides a concise summary of structural models for MGs. **Figure 1** presents a graphical summary of the cluster-based models.

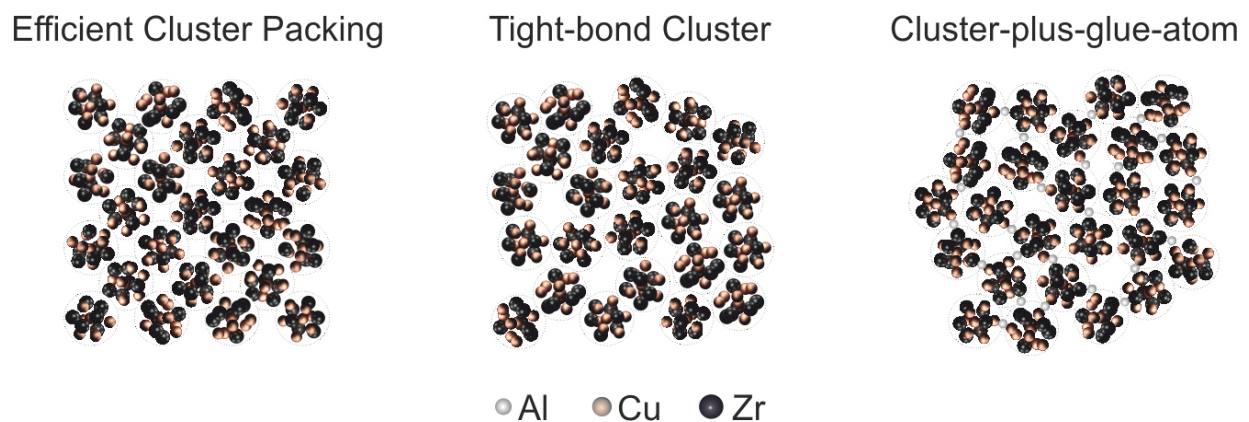


Figure 1. Planar representations of cluster-based structure models for metallic glasses. Left—A $\text{Zr}_{46}\text{Cu}_{54}$ glass consisting of Zr_7Cu_6 clusters² arranged in fcc structure [100]. Middle—A $\text{Zr}_{46}\text{Cu}_{54}$ glass consisting of randomly arranged tightly bonded Zr_7Cu_6 clusters. Right—A $\text{Zr}_{43}\text{Cu}_{50}\text{Al}_7$ glass consisting of randomly arranged Zr_7Cu_6 clusters glued together by Al atoms.

¹ In this context atomic clusters are small particles consisting of up to 200 atoms.

² Notation of clusters: Ag_m indicates a clusters consisting of m Ag atoms; Ag_5 indicates a cluster made out of 5 Ag atoms. In the same way, Zr_7Cu_6 indicates a cluster made out of 7 Zr and 6 Cu atoms.

All these cluster-based models allow short- and medium-range order (up to distances of few cluster sizes), while the disordered nature of MGs on the long-range is retained due to local atomic stresses and topological frustration.

Cluster-based models have been employed by various groups for the interpretation of their experimental and theoretical results. Probably, the best example was delivered by Hirata et al. [24] through nanobeam electron diffraction experiments performed on rapidly quenched $\text{Zr}_{66.7}\text{Ni}_{33.3}$ MGs in combination with *ab initio* molecular dynamics simulations. They have shown that sub-nanoscale-ordered regions can produce distinctly symmetric electron diffraction patterns that originate from individual and interconnected atomic clusters as building blocks of MGs.

Cluster-based structural models have improved our understanding of MGs to a great extent; the positive observations are exclusively limited to searching for and finding of cluster units in MGs and occasionally relating the overall composition of MGs to the composition of observed clusters. One definite knowledge that has emerged as the result of cluster-based structural models is, however, that MGs indeed belong to the category of cluster-assembled materials (CAMs)³. As such, it should be possible to fabricate metallic glasses by putting appropriate clusters together. This approach, which has been neglected till quiet recently for practical reasons as it will be outlined below, is the subject matter of this chapter.

3. The bottom-up approach to MGs

In order to verify the appositeness of cluster-based structural models for MGs, which suggest that metal clusters are the building blocks of MGs, their fabrication by deposition of selected⁴ metal clusters to form cluster-assembled metallic glasses (CAMGs) was recently proposed [25]. In the following sections, we will go into some details about what metal clusters are, and how are they synthesized. Despite the fact that CAMGs are still at a very early stage of their development, they make up the core of this chapter, because they are expected to contribute largely to our understanding of amorphous structure of MGs at the atomic level and also help to decipher the structure–property enigma.

Generation, selection, and deposition of metal clusters are all among the most advanced disciplines of material science. The current state-of-the-art only allows for the fabrication of CAMG samples in form of thin films. This temporary technical limitation, which will probably accompany us for another decade, brings CAMGs very close to thin-film metallic glasses (TFMGs) that also have attracted interest [26].

TFMGs are also fabricated in a bottom-up approach and thus are included in this chapter. However, they will not be at the spot light here, mainly due to the following two reasons: Firstly, in TFMGs, the building blocks cannot be actively altered and controlled as they are always atoms or an undefined distribution of clusters. Consequently, it is not possible to

³ CAMs are materials that are fabricated by assembling atomic clusters i.e. have atomic clusters as their building blocks.

⁴ In this context and throughout the text, selection refers to mass-selection; separation of clusters based on their mass.

actively influence the structure of TFMGs at the atomic level. Secondly, the composition and the building blocks of the films cannot be modified *independently*, so that a correlation between the building blocks and the film properties cannot be established.

Nanoglasses are another class of metallic glasses that are closely related to CAMGs. Introduced by Gleiter et al. [21, 27–29], nanoglasses are generated by sputtering or evaporating the material of choice, and subsequently consolidating the formed glassy droplets into a pellet-shaped sample. Here, only a very vague control on the structure and composition of the droplets may be achieved. There are number of published works on nanoglasses, which deal with them in appropriate details [21, 29, 30].

3.1. Cluster-assembled metallic glasses, CAMGs

Building blocks of CAMGs are metal clusters. In this section, we address generation, selection, and deposition of metal clusters to form CAMGs. Metallic clusters can be generated in metal cluster sources, which will be described briefly in Section 3.1.1. The output of a cluster source is a distribution of neutral and charged clusters, and thus, a selection step (Section 3.1.2) is required to pick out the desired clusters before deposition. Finally, the selected clusters should be deposited on to a support material in order to fabricate CAMG, as will be explained in Section 3.1.3. The three main steps of CAMG fabrication are schematically summarized in **Figure 2**.

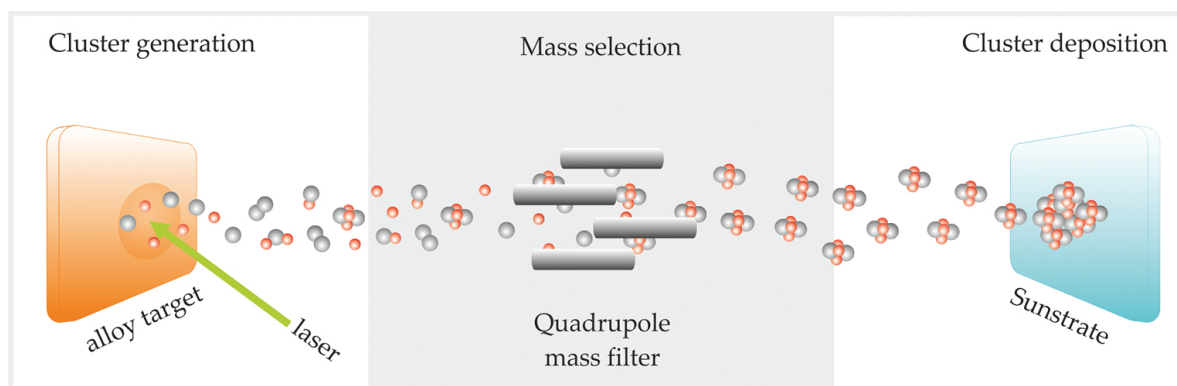


Figure 2. Bottom-up approach to nanofabrication of metallic glasses. Left—mixed metal clusters are generated by laser vaporization of a metal alloy target. Middle—using mass selection, a specific cluster is picked out of the cluster beam. Right—mass-selected clusters are deposited on a support material to form a metallic film.

3.1.1. Generation of metal clusters

The development of cluster sources and subsequently the investigation of clusters, started back in the 1960s with the idea of utilizing the non-equilibrium conditions of an adiabatically expanding vapor, for example, by supersonic expansion⁵ of a gas into vacuum [31, 32]. Cluster

⁵ Supersonic expansion is achieved when a gas expands into vacuum with a Mach number larger than unity.

formation is believed to be due to the supersaturation of rapidly cooled vapor which stimulates homogenous nucleation in the beam [32].

There are various possibilities to produce atomic clusters from bulk materials. Common to almost all these methods is that atoms are firstly ejected from the bulk material and then are brought together to form clusters in the gas phase. A review of all types of cluster sources is beyond the scope of this chapter. Only the laser vaporization cluster source will be introduced here in more detail as this is the only source that has ever been employed for fabrication of CAMGs [33].

The first generation of a laser vaporization cluster source was reported in the early 1980s, at Rice University by Smalley et al. [34]. Many variants of this cluster source have emerged since then. The use of lasers for ablation of material is a very important feature of this kind of cluster source, since it allows for the production of metal vapors of even the most refractory metals such as W and Mo without overheating any part of the apparatus. The supersonic expansion of the cluster beam is the other important feature of this source (also common among other cluster sources). A schematic view of a laser vaporization cluster source is shown in **Figure 3**.

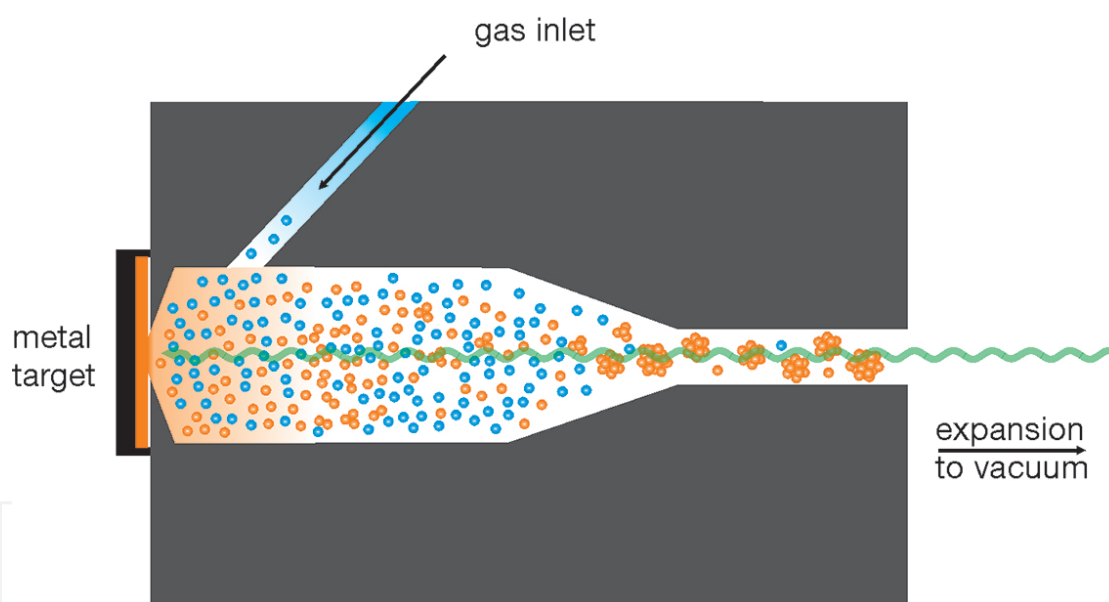


Figure 3. A schematic view of the laser vaporization cluster source is illustrated. A laser beam is focused on to a metal target (either pure metal, or an alloy) in the presence of high pressure of a buffer inert gas. The plume is mixed with the gas and undergoes multiple collisions prior to expansion into vacuum.

The laser vaporization cluster sources produce clusters in the size range from two to several hundreds of atoms per clusters. The vaporized material is cooled by collisions with inert gas atoms which greatly outnumber the ablated metal atoms. The formation of clusters requires three-body collisions between two metal atoms and a rare gas atom (in the case of dimer formation), such that the rare gas atom can take the collision energy away in the form of its kinetic energy and thus make it possible for the metal atoms to stick together without violating the conservation of momentum. This process then needs to be repeated many times to form

larger clusters and that is why higher pressures of the rare gas are required for the generation of larger clusters. The formation of larger clusters can then proceed by either the addition of single atoms to smaller clusters or by merging smaller clusters together.

In most cluster beam facilities, clusters traverse a skimmer after leaving the nozzle. The main function of a skimmer is to collimate the expanded gas mixture that contains the clusters, into a directed cluster beam [35–37]. The cluster beam is then guided further to the mass selection unit before it is deposited.

3.1.2. Cluster selection

The cluster beam that leaves the source contains neutral clusters as well as negatively and positively charged ones. The ion optics used to guide the cluster beam is set to guide either the positive or the negative ions, but it cannot influence the neutral particles. For instance, if negatively charged ions are excluded from the cluster beam through the ion optics, the cluster beam will consist of positively charged ions that are actively guided and neutral clusters that fly in the same direction. In order to exclude the neutrals from the beam, it is common practice to include an electrostatic bender to deflect the charged cluster beam while the neutral beam will not be affected. This separation step is a crucial prerequisite for cluster selection as electrical and magnetic mass filters cannot interact with neutral particles and thus are not able to distinguish among different neutral clusters.

After exiting the deflector, the beam of positively charged clusters is further guided to a mass filter, commonly a quadrupole mass spectrometer, which combines DC and radio frequency AC voltages to select a specific cluster mass from the cluster beam. This is the selection step where a single cluster mass or a collection of masses are selected for deposition. The selection criterion of a quadrupole mass spectrometer is the mass-to-charge ratio of the clusters; the voltages can be set to make the trajectories of clusters that are heavier or lighter than a set mass unstable and thus exclude them from the cluster beam. This selects only those clusters that have a mass within the set mass window while discarding all the others. The width of the mass window can be controlled, and thus, the mass resolution of the device can be adjusted. In general, the mass resolution is set to be just high enough to separate adjacent masses since the transmission of mass filters decreases with increased mass resolution.

The intensity of a cluster beam is commonly evaluated by measuring the current that is caused by charged clusters in the beam. To this end, a Faraday cup⁶ or alternatively a metal plate is used to collect the clusters and the current flowing from the collector to ground upon arrival of clusters is measured over time. The performance of a cluster source can be determined from its cluster distribution by recording a mass spectrum. **Figure 4** presents mass spectra for pure Ag and CuZr alloy clusters generated by a laser vaporization cluster source. The number of clusters in the cluster beam can be deduced from the measured current, dividing the cluster beam current by the elementary charge will give the number of singly charged clusters that have been detected over 1s. For instance, a cluster current of 160 pA translates into $\sim 10^9$ clusters

⁶ Named after Michael Faraday, a Faraday cup is an electrically conductive cup-shaped plate, which is used to collect charged particles under vacuum conditions.

in 1s. For a laser vaporization source with a repetition rate of 100 Hz (100 laser pulses in a second), this means 10 million clusters in each single laser pulse. Although these numbers may sound large, much higher cluster currents are required for deposition purposes, as will be explained in the next section.

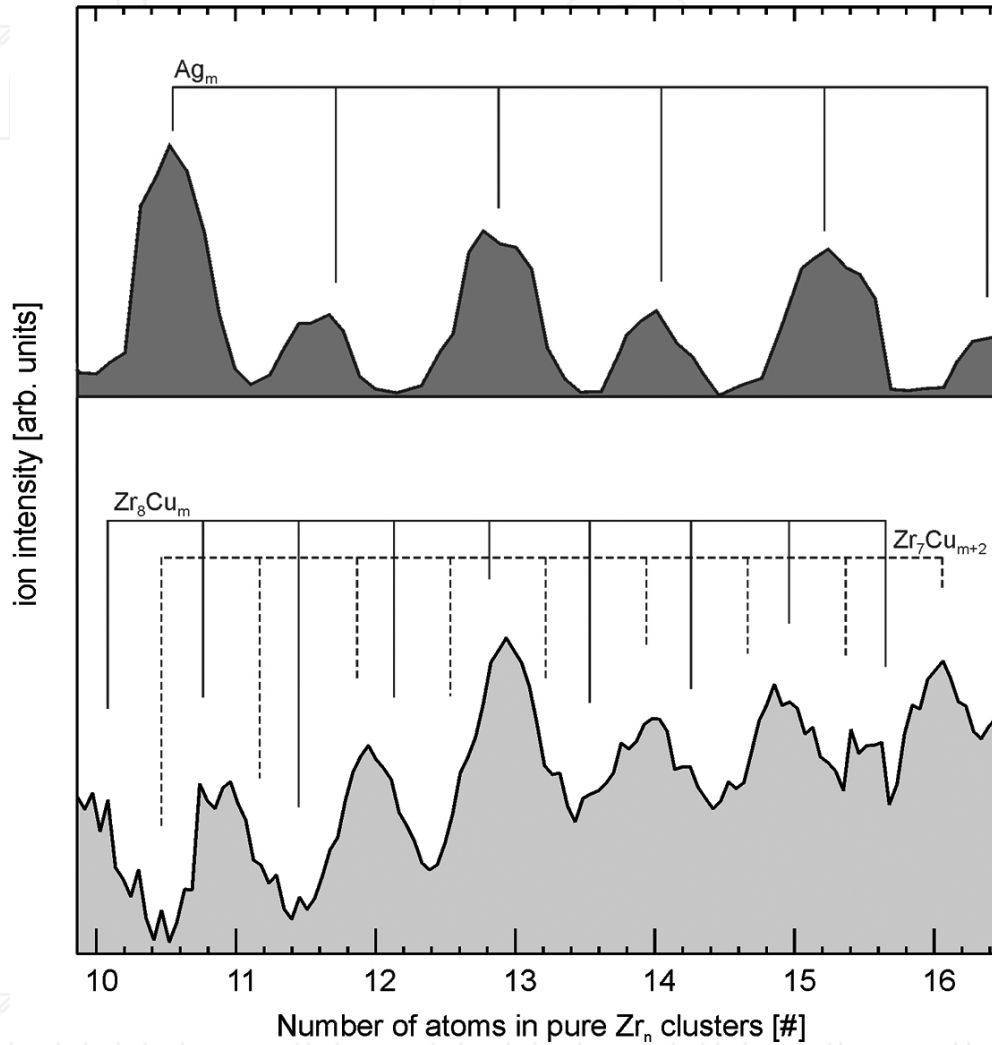


Figure 4. Mass spectra of pure silver clusters (top) and mixed CuZr cluster (bottom) generated by a laser vaporization cluster source are shown. The mass resolution of the quadrupole mass filter is identical for both cases. While in case of silver clusters, the ion peaks are clearly separated, for CuZr clusters peaks cannot be resolved due to the overlap between the masses of mixed clusters plus the fact that Zr with four and Cu with two naturally stable isotopes further broaden the spectrum. In the top, Ag_m^+ clusters⁷ with $m = 9-14$ are observed. The higher intensity of clusters with odd number of atoms is due to their higher stability based on their electronic structure. Such odd-even stability oscillation is common to 1s metals. In the bottom, mixed Zr_nCu_m^+ clusters of various compositions are observed while the spectrum is dominated by pure Zr clusters. Two series of Zr_nCu_m^+ ($m = 3-11$) clusters are assigned. The Zr_{13}^+ cluster peak is clearly more intense than other clusters in the mass spectrum. Here, the geometry of the icosahedral clusters with 13 atoms is the stabilizing factor.

⁷ Notation of clusters: Ag_m indicates a clusters consisting of m Ag atoms; Ag_5 indicates a cluster made out of 5 Ag atoms. In the same way, Zr_7Cu_6 indicates a cluster made out of 7 Zr and 6 Cu atoms.

3.1.3. Cluster deposition

After cluster selection, the selected clusters should be deposited onto a support material. Collision with surface may lead to fragmentation of the clusters and render the selection step obsolete. Accordingly, special care should be taken to achieve *soft-landing* conditions when depositing clusters. The material used as support is, therefore, very important. If a conductive support material is used, soft-landing can be easily achieved by applying a voltage to the support to slow down the arriving ions to kinetic energies lower than 0.5 eV per atom (lower than 2 eV for a cluster consisting of 4 atoms or lower than 5 eV for a cluster consisting of 10 atoms and so on). If on the other hand a non-conductive material is used, no adjusting voltage can be applied and the energy of the ion beam should be adjusted by tweaking the ion optics so that the kinetic energies of the ions are low enough to guarantee soft-landing.

Another issue regarding the conductivity of the support material is related to the charge of the clusters. As discussed in Section 3.1.2, clusters are selected based on their mass to charge ratio and thus only charged clusters are suited for mass selection. While the ions will lose their charge once deposited onto a conductive surface, they will keep or only partially lose their charge while in contact with an insulator surface. Consequently, a neutralization mechanism is required to avoid interruption in deposition due to electrostatic repulsion. Due to this effect, almost exclusively positively charged clusters are used for deposition purposes, since they can be neutralized by an electron beam, whereas a proton beam would be required for neutralization of negatively charged clusters.

The other aspect regarding the choice of the support material is its atomic structure, that is, whether it is crystalline or amorphous. Amorphous supports are preferred because they will not provide periodic nucleation sites and thus will not promote the rearrangement of clusters and crystallization of the film. However, as it will be shown in Section 4.1., having an amorphous substrate complicates the structural characterization of CAMGs. The Support material may also be cooled down in order to suppress diffusion of clusters and to enhance the glass forming probability by stopping the clusters from undergoing large geometrical deformations.

As already mentioned in the previous section, high cluster currents are required for deposition of CAMGs. To further illuminate this issue, we may use the following example: A cluster beam can be focused down to a round spot with a diameter of 0.2 cm. Using such a beam to deposit clusters on to a support will result in a coated area of $\sim 0.125 \text{ cm}^2$, the so-called cluster spot. An icosahedral cluster of 55 atoms (one of the largest clusters relevant for MGs) will have a diameter of $\sim 2 \text{ nm}$ and thus cover an area of $\sim 12.5 \text{ nm}^2$. Filling a single layer (2-nm-thick film) of the cluster spot with the total area of 0.125 cm^2 , with such clusters will demand $\sim 1 \times 10^{12}$ clusters (for this estimation, the free space between touching spherical clusters was neglected which leads to $\sim 10\%$ overestimation of the number of clusters). In order to get a 1- μm -thick film, at least 500 times more clusters should be deposited. Now assuming a cluster beam current of 160 pA, about 139 h of deposition will be required. Obviously, an enhancement of at least an order of magnitude in cluster beam current is necessary to have a feasible deposition time. Such high cluster beam currents are above what can currently be achieved using state-of-the-art laser vaporization cluster sources, and consequently, the only reported CAMGs to date have used a relatively broad collection of clusters and not an absolutely selected beam of

a single cluster mass. **Figure 5** depicts a cluster deposition facility incorporating all its components.

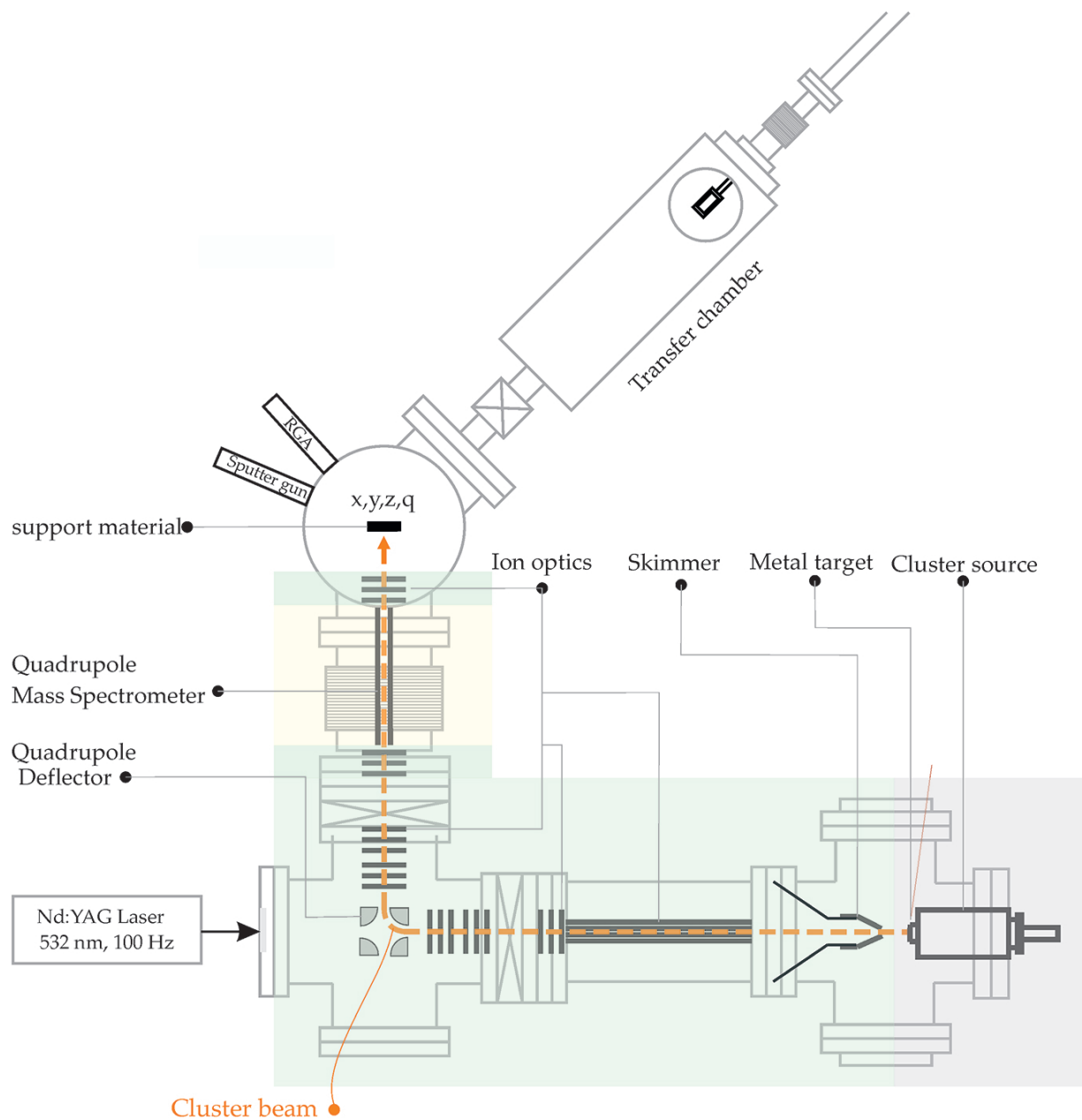


Figure 5. A schematic view of a cluster deposition facility is depicted. The facility is composed of a laser vaporization cluster source (grey shade), set of ion optics before and after mass selection (green shade), mass selector (yellow shade), and a deposition chamber (unshaded). The deposition chamber is further equipped with a sputter gun for cleaning the surface of the support material prior to deposition, a rest gas analyzer (RGA) for monitoring the quality of the vacuum in this chamber, and a transfer chamber for sample handling purposes such as removing the sample from this facility for transport to other facilities for analysis and characterization. The dashed orange line shows the path of the cluster beam from the cluster source through the ion optics and the mass filter down to the deposition chamber where clusters are soft-landed onto the support material.

3.2. Thin-film metallic glasses TFMGs

Driven to examine the relation between the heat of hole formation and crystallization temperature in amorphous alloys, Nastasi et al. [38] fabricated probably the first thin-film metallic glass in binary systems of Cu–W and Cu–Ta just couple of years after the very first TFMG in La–Au system achieved by solid-state amorphization, where it was also showed that deep eutectics are not a necessary criterion for glass formation in metallic alloys [39]. Currently, TFMGs are commonly fabricated by co-deposition of multiple metals either from an alloy target or multiple targets where the flux of each component can be controlled separately. Zr-based alloys are the most studied systems to date.

Interest in TFMGs is fueled by their distinct properties even compared to counterpart MGs, such as broader glass forming range and higher strength [26, 40–42]. Their broad and continuous glass forming range leads to tunability of their properties by simply adjusting their composition [26]. Their potential application as bio-coatings further increases their relevance. Recently, the corrosion resistance of binary Zr–Ni and Zr–Co TFMGs was investigated [43]. Although TFMG enjoys a great technical significance, they will not play a momentous role in unraveling the structure–property puzzle in MGs.

In the case of TFMGs, the gas phase entities used for fabrication of metallic films are mainly atoms and not atomic clusters. Even if some clusters are available in the deposition beam, up to now no control on the structure and composition of the building blocks could be achieved. Moreover, beside the case of atomic deposition, no information on the properties of the structural units that build up the films has been accessible. In contrast, in the case of CAMGs, atoms are very often deliberately excluded from the deposition beam and only clusters are used to build up a metallic film. The main advantage of CAMGs over TFMGs is that the building blocks can be altered while keeping the composition of the resultant metallic film unchanged.

4. Structure–property relation in CAMGs

In previous sections, CAMGs were introduced and their fabrication using cluster beam technology was described. Here, we will have a closer look on how the study of CAMGs serves to explore the structure–property relation in MGs. Using the example of $\text{Zr}_{50}\text{Cu}_{50}$ alloy, we will demonstrate this capability. Employing the aforementioned cluster beam technology, a $\text{Zr}_{50}\text{Cu}_{50}$ film can be fabricated using many different combinations of various clusters as building blocks. The possibility of having the same composition composed of different building blocks is a unique feature of CAMGs. Investigating the properties of these films in comparison with a rapidly quenched MG of the same composition will be a key step in understanding the structure of amorphous alloys and thus the structure–property relation in amorphous metals. On the other hand, comparing the properties of CAMGs with the properties of metal clusters used for their fabrication will reveal the nature of interactions among metal clusters when forming an extended material. Furthermore, looking at the local structure

of CAMGs will unravel the extent of structural deformation that metal cluster undergo as building blocks of CAMGs. **Figure 6** summarizes the different aspects of this approach.

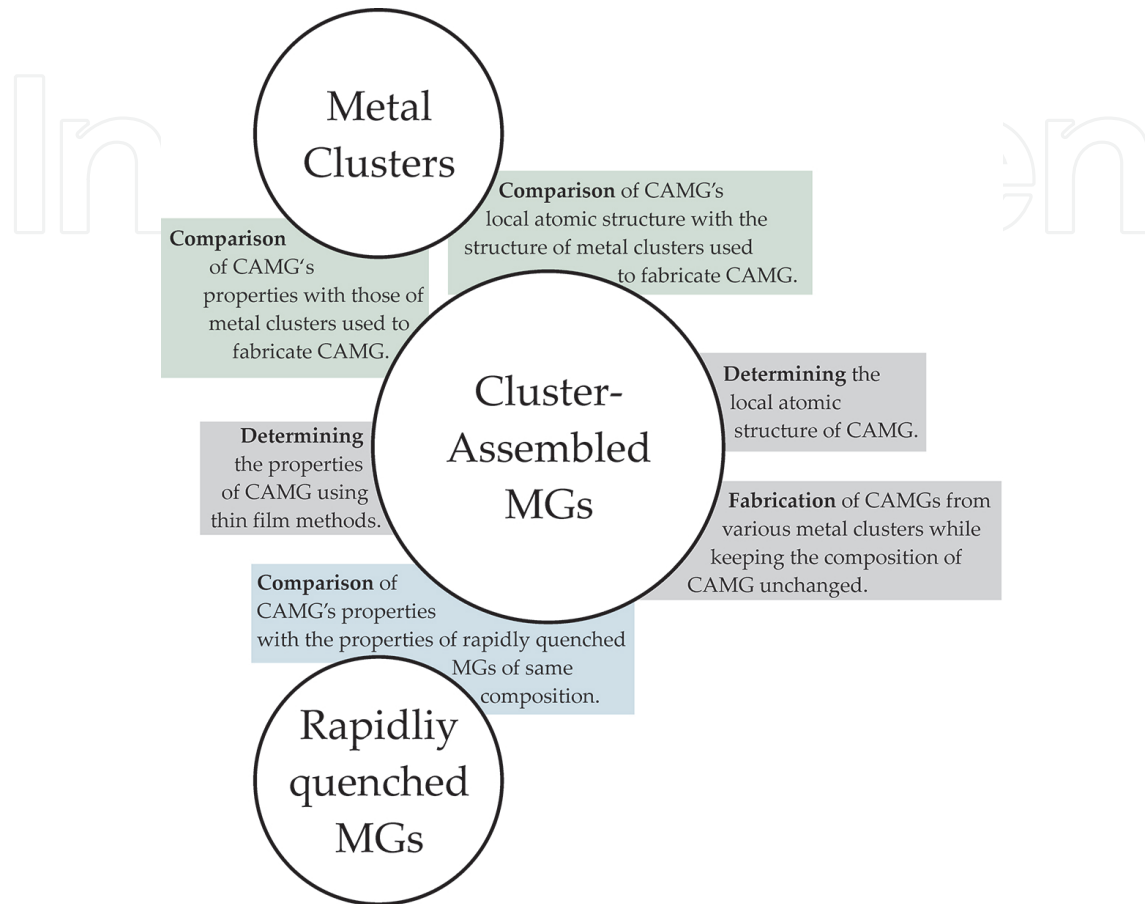


Figure 6. The scientific approach of utilizing CAMGs is presented. After fabrication of CAMGs from specific metal clusters as building blocks, their structure and properties should be determined. On the one hand comparing the properties of CAMGs with the properties of rapidly quenched MGs with identical composition will provide us with information on the structure of rapidly quenched MGs in relation to the metal clusters: the closer the properties of CAMGs and MGs, the closer their structures are! On the other hand, comparing the properties of CAMGs with the properties of their constituent metal clusters will reveal the nature of inter-cluster interactions. Further, by comparing the local atomic structure of CAMGs with the structure of their constituent metal clusters, the degree of deformation and stability of metal clusters while performing as building blocks of MGs can be deduced.

It will not be practicable to consider all the possible combinations. Instead, let us choose some representative combinations to provide a more clear idea about the benefits of CAMGs. Consider the following four scenarios:

1. the film is fabricated by deposition of equal number of Zr_{13} and Cu_{13} clusters.
2. the film is fabricated by deposition of equal number of Zr_7Cu_6 and Zr_6Cu_7 clusters.
3. the film is fabricated by deposition of a set of clusters in the mass range between 400 and 2000 amu, including pure Zr and Cu clusters with more than 4 and 7 atoms, respectively,

and all the mixed clusters with a mass within that range, so that the overall stoichiometry of the film remains is not violated (Atoms and smaller clusters are deliberately excluded).

4. the film is fabricated by deposition of $\text{Zr}_{10}\text{Cu}_{10}$ clusters.

For all of the above-mentioned hypothetical films, the composition is the same; however, they will possess different atomic structures unless the building blocks are strongly deformed and are highly flexible in sharing atoms among each other. Considering the four different scenarios introduced earlier, only the third scenario (using a set of cluster within a mass range) has been realized experimentally [33] and will be presented in the next section as a proof of principle.

4.1. Zr–Cu CAMGs: the first steps

The first attempt to apply cluster beam technology for fabrication of metallic glasses was undertaken recently using binary Zr–Cu alloys [33]. The justification for this choice is threefold. Firstly, Zr–Cu binary system shows high glass forming abilities (GFA) in a wide range of compositions [44–46]. Secondly, a large body of literature on Zr–Cu MGs and TFMGs exists, which proved to be essential in interpretation of the experimental observations [44–59]. And thirdly, cluster generation and cluster selection of mixed metal clusters become more difficult with increasing the number of elements in the cluster, and thus, a binary system is the logical starting point.

Metallic $\text{Zr}_{50}\text{Cu}_{50}$ films were fabricated by deposition of a set of clusters having masses between 350 and 2000 amu (scenario Nr. 3) on silicate glass substrates, under ultrahigh vacuum, and soft-landing conditions. Films of various thicknesses ranging from 33 to 600 nm were produced. At this stage, the structure and properties of the clusters used to assemble the metallic film are not available. However, all properties of metal clusters can be obtained in state-of-the-art cluster laboratories including their optical, magnetic, chemical, catalytic, electronic, and structural properties. The first question to be answered while fabricating CAMGs for the first time is, however, whether the synthesized film is in an amorphous state at all. Surface X-ray diffraction at the European Synchrotron Radiation Facility (ESRF) was used to answer this question. The details of the experiments and sample preparation are available elsewhere [33]. Here, the most important findings underpinning this bottom-up approach are briefly summarized.

Figure 7 depicts the diffraction pattern of the first cluster-assembled Zr–Cu MG. Despite the interference caused by the broad diffraction band of the silicate glass support, a clear halo peak, which corresponds to a scattering vector of 27.43 nm^{-1} , is observed in excellent agreement with literature values for $\text{Zr}_{50}\text{Cu}_{50}$ MGs determined from high energy XRD, neutron diffraction, and extended X-ray absorption fine structure (EXAFS) spectroscopy [60]. Accordingly, it could be unambiguously concluded that the fabricated cluster-assembled metallic film is in a glassy state. This observation alone is sufficient to prove the practical feasibility of employing cluster beam technology to form CAMGs.

The good agreement between the observed scattering vector and the literature value may suggest that the structure of the Zr–Cu CAMG is very close to that of rapidly quenched samples. However, it should be noted that the position of the first XRD halo is not very sensitive

to the atomic structure of amorphous metals [61]. In fact, there is almost no difference in peak position for amorphous solids and their corresponding liquids.

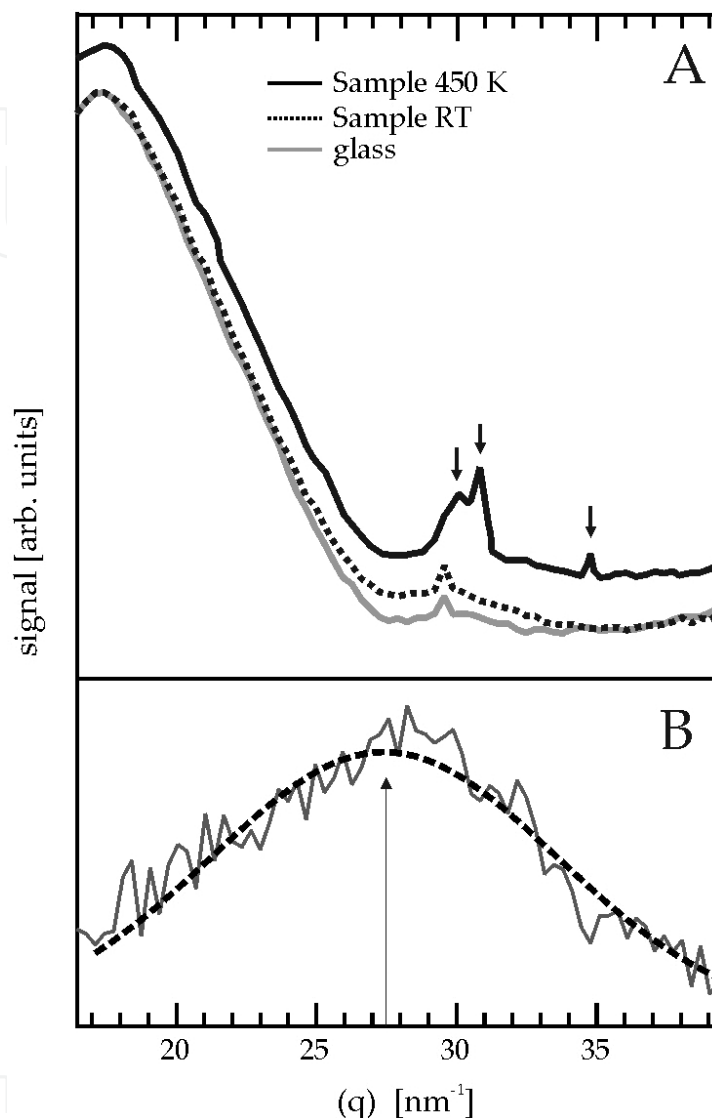


Figure 7. (A) Diffraction patterns of borosilicate glass (solid grey line), cluster-assembled film at room temperature (dashed line), and cluster-assembled film after annealing at 450 K (solid black line) are shown. The arrows indicate the position of the peaks that emerge as a result of annealing. (B) By subtracting the glass signal from the signal recorded for cluster-assembled film, a halo peak is observed that can be fitted by a Gaussian (dashed line). The position of the peak in scattering vector is in excellent agreement with literature values for Zr–Cu MGs of the same composition.

Crystallization temperature, T_x , is a more sensitive probe for the structure. As shown in **Figure 7**, annealing the Zr–Cu CAMG at 450 K for 580 s leads to emergence of sharp crystalline peaks in the diffraction pattern that were not there prior to heat treatment. These diffraction peaks belong to fcc Cu and bcc CuZr phases [33]. The crystallization temperature of Zr–Cu MGs is much higher than 450 K (about 200–300 K higher), which points to the structural

difference between rapidly quenched samples and the glassy film fabricated from metal clusters. A reasonable explanation for the lower T_x of Zr–Cu CAMG under discussion could be based on an increased degree of structural disorder caused by the diversity of metal clusters used to fabricate the film. In Fact, lowering the degree of short-range order is known to lead to the decrease of T_x in glasses [62].

Although the existence of an amorphous $Zr_{50}Cu_{50}$ phase in the fabricated CAMG could be confirmed, the broad range of metal clusters used to produce the amorphous film detains any detailed analysis of the relation between the structure of the film and its constituent building blocks. The example provides a very promising first step in a rather long journey of mostly unforeseeable challenges. Some of the upcoming challenges, however, can be expected, and a number of research groups are working on solving them. The most immediate next steps that have to be (are being) taken in this road are briefly listed in the next section.

4.2. The next steps

Having demonstrated the feasibility of CAMG fabrication using a diverse set of clusters in the Zr–Cu binary system, and the next steps can be taken in three directions of different nature. The first and probably the most important technical issue is the improvement of cluster sources. As described in Section 3.1.3, much higher cluster currents are needed if specific single clusters should be picked out for the deposition of designed CAMGs. Since the cluster science community is continuously engaged in enhancing the performance of the cluster sources, we strongly anticipate that this and other technical issues will be resolved in the near future.

The second communicational issue is the lack of information on clusters relevant for MGs. Scientists working on MGs and metal clusters have not been in any close contact and the information flow between these two fields has been suffering. Yet there is more than enough motivation from both fronts to come together and hopefully put an immediate end to this disconnection. On the one hand, cluster science community is highly interested in understanding cluster–cluster interactions and expanding the borders of the cluster science to more complex clusters. Further, departure from mainly purely fundamental science and moving toward real application by developing cluster-assembled materials (CAMs) has been a long-term goal of cluster scientists. On the other hand, the vision of getting to an atomic structural model which can be verified through CAMGs, and eventually solving the long standing structure–property puzzle has already triggered enthusiastic activities among material scientists. Although not many individuals have been active across the borders of the two fields, an enthusiastic collective interest that has been missing in the past is currently emerging.

The third issue is related to the handling of CAMGs and their characterization. Currently, none of the cluster deposition facilities around the world and the equipment for thin film and MG characterizations are in the vicinity of each other. This requires complicated sample handling endeavors, which are not always compatible with the metastable state of CAMGs. For instance, in the case of the CAMG treated in Section 4.1, the sample transfer from the cluster deposition facility to the apparatus where its structure was studied has been a challenge, which could have been fully avoided by having a cluster deposition facility present at ESRF. We consider this issue less critical because we believe as soon as the other two issues are resolved (even

partly), the interdisciplinary collaborations will naturally lead to emergence of (many) such laboratories.

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