Formation of Non-equilibrium Alloys Through Nanocluster Deposition: The Ag\(_{0.3}\)Al\(_{0.7}\) Supersaturated Alloy

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Abstract
We present here results of soft landing 4 nm sized clusters of Ag from a nanocluster beam on Al for 5 mins and 15 mins. We have studied the samples after cluster deposition using X-ray Photoelectron Spectroscopy, Secondary Ion Mass Spectroscopy, and X-ray Diffraction. We have found that no Ag nanoparticles have formed, the Ag is not oxidised but the Al has undergone some hydrated oxidation. More important, we have established the formation of the supersaturated Ag\(_{0.3}\)Al\(_{0.7}\) alloy with an fcc structure at ambient temperature and at Ag concentrations \(~0.1%-0.2%\) of the total atoms in the sample, for both the 5 min and 15 min irradiated samples, growing with the same orientation as the Al lattice, with traces of another phase suggestive of the hcp phase of Ag\(_2\)Al. Interestingly, the crystallinity of the alloy in both cases is better than that of the Al lattice and they have a marginally lower strain. We have proposed an explanation of the strong tendency to form Ag-rich alloys by invoking a recently established structure of Al with very low bonding electron density localised at the tetrahedral interstices.

Keywords: Non-equilibrium alloys, Nano-cluster beam deposition, Ag-Al Alloys, SIMS, XPS, XRD.

1. Introduction
There exist a number of non-equilibrium alloys. If we start with the immiscible metals, there are, for example, the alloys of Mo and Cu \([1]\), Au and Ni \([2]\), etc. Again, the Cu\(_3\)Au alloy with the \(\text{DO}_{23}\) metastable structure in place of the stable face centred cubic or \(\text{fcc (L1}_2\)\) is a non-equilibrium alloy formed at interface of Cu and Au when the latter is sputtered on the former \([3]\). For Au and Ni, we find that the majority of the phase space is occupied by a region where the single phase is unstable and both phases coexist – the so called ‘miscibility gap’ \([4]\), which disappears for Au-Ni alloys prepared through non-equilibrium processes and a single phase alloy is obtained at all compositions \([2, 5]\). Besides the obvious advantage of producing such alloys with distinctly new properties that can have excellent potential for application \([6]\), these alloys, unlike glass, can have well-defined structures and bonds, and thus can provide answers to specific and fundamental questions on the non-equilibrium growth process itself.
The phase space of alloys of Ag and Al is surprisingly complex and rich [7] in view of the fact that they have almost identical fcc lattices with a very small difference in the lattice constants. Though the phase space has been studied since the 1920s [8-11] yet the exact reason behind this complexity has not been clarified. The Al-rich part of the phase space consists an alloy with an fcc structure, without formation of any stoichiometric bimetallic compound, and with composition varying from a minimum of 1.1% atomic of Ag to a maximum of 23.5% atomic at 567°C. Above this the fcc phase of the alloy becomes unstable and an immiscibility gap opens up [7], with co-existence of the fcc phase and the hcp phase [7,9] with an Ag-rich and fixed (Ag2Al) [12] composition. Inside this immiscibility gap there are the Guinier-Preston zones [8] formed by precipitation transformation [13], where the excess Ag in the supersaturated fcc alloy segregates to form the Ag2Al phase. The fact that in the Al-rich part of the phase space there are no stoichiometric bimetallic compounds whereas there are a number of bimetallic compounds, namely, the different structural phases of Ag2Al and Ag3Al, in the Ag-rich part, shows a clear asymmetry in Ag-Al bonding in these two regions.

In this paper we have probed the Ag-Al system under non-equilibrium conditions. We have carried out deposition of Ag on Al by ionized cluster beam deposition. A unique aspect of this technology is its size-selected clusters deposition at energy close to zero, i.e. at the soft-landing approximation. This method produces a continuous and intense cluster beam, where an atomic vapour is produced by a magnetron sputtering unit [14], to fabricate nanocluster films both for basic research [15-17] and technological applications [18-21], as it is possible to retain the shape and size of the nanoclusters after deposition [22]. On deposition of clusters over a substrate, the clusters may equilibrate by diffusion [23], aggregation or fragmentation [24] depending on the substrate. Here we have deposited size-selected Ag-nanoclusters of diameter 4 nm on Al surface at a very low energy. Our interest was to know (1) whether the nanoclusters remain as clusters or form alloy with the Al at ambient temperature and, if the latter, (2) what is the alloy structure and composition? In particular, we wanted to know if even with such small amounts of Ag and at the non-equilibrium conditions prevailing, whether the tendency of forming Ag-rich phases is retained.

Ag-Al alloys are finding application in a wide variety of technological fields due to their high current capacity at high temperatures, a combination of the high conductivity of Ag and the low thermal coefficient of resistance of Al [25]. The hcp Ag2Al phase is found to act as a self-healing structure dispersed within the fcc matrix [26] in the supersaturated alloy. Wetting of Si surfaces by Al serves to attach Ag-Al alloy nanoparticles is used as plasmon-confining coating in solar cells [27], as also in perovskite solar cells [28].

2. Deposition of Ag atomic clusters in the Al substrates

Figure 1 shows the schematic diagram of the nanocluster ion source, the formation and mass selection of clusters. In our cluster source, a magnetron is used to produce Ag-vapour using sputtering by Ar+ ions. This also produces energetic Ag vapour comprising small clusters of atoms and ions, which moves toward a region cooled by chilled water or liquid N2 (LN2) called aggregation zone. The magnetron is placed on a linear drive which enables it to be moved to vary the volume in the aggregation zone. The cluster size is controlled by this volume and the residence time of the clusters inside this region. The magnetron can work in both DC and Radio Frequency (RF) mode which enable us to produce metallic or conducting as well as insulator or semiconductor nanoparticles [29] or nanoclusters.

Base pressure in main deposition chamber was kept at 1.7×10⁻⁸ mbar and base pressure in the cluster chamber was at 5.4×10⁻⁴ mbar. During experiment pressure in main deposition chamber was at 1.5×10⁻¹ mbar and cluster chamber pressure was at 2.3×10⁻¹ mbar. The magnetron voltage was 308.4 V and current was 0.126 mA, while cluster beam current was ~1 nA. Size-selected Ag nanoclusters of diameter ~4 nm (n~1750) were produced and deposited with narrow mass width on 99.999% Al substrates (Alfa Aesar) of dimensions 10 mm×10 mm×0.5 mm for 5 mins (sample S5) and 15 mins (sample S15). Substrate was kept at room temperature (~30°C) during deposition. In estimating the
size of a large cluster, often a cluster is considered as a liquid drop \([30,31]\) or a compact solid so that its density is comparable to that of a macroscopic solid \([32]\). Then the radius of the cluster with \(n\)-atoms can be expressed as, \(r = r_w n^{1/3}\), where \(n\) is the number of atoms in the cluster and \(r_w\) is the Wigner-Seitz radius (for Ag, \(r_w = 0.166\) nm), which brings the radius of clusters to 2.00 nm.

**Figure 1.** Schematic diagram of size-selected nanocluster deposition system

### 3. X-ray Photoelectron Spectroscopy

The elemental composition and the electronic states of the elements present in S15 were determined by X-ray photoelectron spectroscopy (XPS). XPS of the sample was performed in a PHI 5000 VERSAPROBE II scanning microprobe (M/S. Physical Electronics, USA) with non-monochromatic Al K\(_\alpha\) (1486.6 eV) X-ray source operating at 15kV and 25 W and with probe size of 10 \(\mu\)m. Collected XPS peak profiles were fit with deconvolutions of Gaussian functions.

**Figure 2.** X-ray Photoelectron Spectra of Al with 15 min of Ag nanoclusters beam deposition on its surface at (a) 2p state of Al and (b) 3d state of Ag. Individual peaks fit with Gaussian functions in green (a) and the overall peak profiles fit with the convolution of the functions (red). Please see text for more details.
Table 1. X-ray Photoelectron Spectroscopy results of Al with 15 min of Ag nanoclusters beam deposition on its surface

| State  | Binding Energy (eV) (15 min Ag) | Assignment                                               |
|--------|---------------------------------|---------------------------------------------------------|
| Al2p   | 72.74, 73.07, 74.91             | Al 2p\textsubscript{1/2} (72.7), Al 2p\textsubscript{3/2} (73.0), Al(OH)O (75.0)\textsuperscript{33} |
| Ag3d   | 369.43, 377.19                  | Ag 3d\textsubscript{5/2} (369.0), Ag 3d\textsubscript{3/2} (375.25)\textsuperscript{34} |

Figure 2 and Table 1 summarise the results of the XPS analysis. The data shows peaks in the 70-80 eV and 350-380 eV ranges, corresponding to the 2p band of Al and the 3d band of Ag, respectively. The three peaks in the first range, namely 72.74 eV, 73.07 eV, and 74.91 eV, can be assigned to Al 2p\textsubscript{1/2}, Al 2p\textsubscript{3/2}, and Al(OH)O, respectively, providing evidence for the formation of hydrated Aluminium Oxide on the Al surface, while Al\textsubscript{2}O\textsubscript{3} is absent. In the second range, the two peaks at 369.43 eV and 377.19 eV correspond to, respectively, the Ag 3d\textsubscript{5/2} and 3d\textsubscript{3/2} states. No signature of oxides of Ag can be observed. Hence, apparently Ag remains in metallic state within the Al matrix.

4. Secondary Ion Mass Spectroscopy

Secondary ion mass spectroscopy (SIMS) for the surface analysis of both S5 and S15 was carried out using a quadruple mass spectrometer-based SIMS instrument (HIDEN Analytical Ltd., UK). The base pressure was of the order of 2.3 x 10\textsuperscript{-7} mbar. The samples were investigated with 4kev O\textsuperscript{2+} primary ions with 25nA current.

![Graph](image)

Figure 3. Secondary Ion Mass Spectra of Al irradiated by Ag nanoclusters beam for (a) 5 mins and (b) 15 mins. Al, Ag\textsubscript{0.3}Al\textsubscript{0.7}, and Ag signals are shown. Please see text for more details.
The results of the SIMS studies on S5 and S15 are summarized in Figure 3(a) and 3(b), respectively. Due to lack of flatness of the sample surfaces, the craters created by the ion beam could not be measured accurately and thus the spectra are plotted against the time of irradiation of the samples by the ion beams instead of the depth of the mass species from the surface.

Nevertheless, the results are unambiguous in detecting the formation of a species with the nominal composition of $\text{Ag}_{0.3}\text{Al}_{0.7}$, besides the expected signature of Al. It is to be noted that signatures of pure Ag are very weak and noisy, confirming the very small amounts of Ag introduced. The vertical dotted lines demarcate the surface region. It can be seen that the bimetallic species is formed a little below the surface in S5 whereas it occupies the entire surface region for S15, besides the expected lower count in the former. This is about 300 while for S15 it is about 1000, i.e., one-third of the latter exactly matching with the cluster deposition time ratio. It is also to be noted that Field Emission Scanning Electron Microscopy (FESEM) and Ultraviolet-Visible Spectroscopy in reflection mode could not detect any Ag nanoparticles.

5. X-ray Diffraction

![X-ray Diffraction Pattern](image)

Figure 4. X-ray Diffraction Pattern recorded for Al irradiated by Ag nanoclusters beam for (top) 5 mins and (bottom) 15 mins.

The X-ray diffraction spectra of the samples were recorded in a XRD diffractometer (Rigaku) operating at 40kV and 40 mA of Cu Kα radiation. The XRD data were collected at step size 0.2° in 2θ and at 1s intervals from $15^\circ$-$85^\circ$. XRD patterns of both samples (Figure 4), of course, show the overwhelming presence of Aluminium (Al) in the fcc-phase having space group $Fm-\overline{3}m$. However, instead of the (111) reflection at 38.5°, the (200) reflection became the 1st order reflection at 44.8°, showing that the sample is cut from a crystal with [200] orientation.
Figure 5. X-ray Diffraction pattern for Al irradiated by Ag nanoclusters beam, around the strongest peak. Peaks for the Al lattice (green), alloy formed after 5 mins (red) and after 15 mins (blue) of irradiation.

In Figure 5 we see that the Bragg peak splits into a main peak (green) belonging to the Al lattice and another peak that shifts to lower angles with deposition time, indicating an expansion in the Al lattice, a signature of Ag atoms going into the lattice, where the peak intensity of S15 (blue) is higher than S5 (red) but there is very little relative separation between them indicating almost the same lattice structure. This structure has been identified as the fcc structure found for the non-stoichiometric Ag$_{0.3}$Al$_{0.7}$ composition in the miscibility gap [8]. The values of cell parameters, unit cell volume, average crystallite size and average lattice strain of cubic Al phase were estimated for these samples from X-ray diffraction (XRD) line profile analysis using Rietveld analysis [35,36] by X’pert high score plus software (PANalytical) [37] and the values are shown in the Table 2. There are two points to be noted from Figure 5 and Table 2, the alloy lattice follows the Al lattice in orientation and, more interesting, it has better crystallinity and lower strain than the latter. It is also found that S5 and S15 contain $\leq 0.1\%$ and $\leq 0.2\%$ of Ag (atomic % of the entire sample). The quality of the fittings of observed diffraction patterns with the simulated patterns are shown by difference plots in Figure 6 for the sample S5.
Figure 6. XRD pattern and difference plot of the sample S5 as obtained by Rietveld technique.

It is also to be noted from Figure 7 that there are very weak peaks that could not be exactly assigned. The clearest of them are at around (a) 40.2° and (b) 82.4°, close to the (101) and (112) reflections of the hcp phase of Ag$_2$Al [38], as was first seen in the miscibility gap [9].

Figure 7. XRD peaks at (a) 40.2° and (b) 82.4° from S5 (black) and S15 (red) close to the (101) and (112) reflections of the hcp phase of Ag$_2$Al.
Table 2. Values of cell parameters, cell volume, average crystallite size and average lattice strain

| Sample      | Unit Cell parameter | Unit Cell volume | Average crystallite Size and Lattice strain of Cubic Al phase |
|-------------|---------------------|------------------|-------------------------------------------------------------|
|             | $a$ (Å)             | $V$ (Å$^3$)      | Crystallite Size (Å) | Lattice strain (%) |
| Ag$_{0.3}$Al$_{0.7}$ | 4.0539             | 66.6238          | 1782.8             | 0.018              |
| Ag$_{0.3}$Al$_{0.7}$ | 4.0542             | 66.6394          | 1250.9             | 0.010              |
| Al          | 4.0526              | 66.5601          | 1075.0             | 0.022              |

6. Discussions

We thus find that (1) an alloy with the composition Ag$_{0.3}$Al$_{0.7}$ is formed (structure shown in Figure 8(a)) in the Al substrates on injecting Ag nanoclusters into them even for the short interval of 5 mins and (2) this alloy has an $fcc$ structure that shows almost no change as the injection time is raised threefold to 15 mins, showing thereby that it is quite stable as is also evident from its identification of a structure in the equilibrium phase space, though in the miscibility gap. This alloy grows with the same crystal orientation as the substrate and has in fact better crystallinity and less strain than the Al lattice. There are also traces of another phase of Ag-Al alloy that could not be identified exactly but may possibly belong to a highly strained form of the $hcp$ phase of Ag$_2$Al (structure shown in Figure 8(b)).

![Figure 8. Structural models of (a) Ag$_{0.3}$Al$_{0.7}$ (face centred cubic) and (b) Ag$_2$Al (hexagonal close packed). The former has been generated using the Mercury freeware from Cambridge Crystallographic Data Centre with the structural data of Table 2 while the latter is from ref 43.](image)

These results bring out more strongly the tendency of forming relatively Ag-rich phases in Ag-Al alloys. We find that even when the overall presence of Ag in Al is less than 0.1%, instead of a very Al-rich alloy, a supersaturated $fcc$ alloy is formed, perhaps even with the presence of the first Ag-rich bimetallic phase ($hcp$ phase of Ag$_2$Al). This tendency and the better crystallinity of the alloy clearly show that bonding with Ag tends to lower the free energy of the Al lattice below its equilibrium ground state.

In this context it is interesting to note that even with three electrons in its outermost s and p sub-shells, Al has a remarkably low binding electron density ($\sim$0.05 eÅ$^3$, more than an order of magnitude lower
than that in graphene, ~0.65 eÅ\(^3\)) and that the bonding electron density is centred entirely in the tetrahedral interstices of Al [39,40]. The binding energy per atom calculated for a 55-atom cluster of Al with an fcc structure is 3.1 eV [41]. On the other hand, for Ag with a single s electron, the calculated binding energy per atom for a 8-atom cluster is 1.42 eV [42]. Hence Al atoms have less than half mobility of the Ag atoms and the Al lattice is largely vacant with much localised electrons. This situation may cause the Al to act as an electron acceptor and the Ag as a donor, to fill the electron vacancies and thus cause a more delocalised electron distribution leading to a more stable structure. We propose this as a plausible explanation of the strong tendency of Ag-rich Ag-Al alloys to form.

7. Conclusion

We have shown that non-equilibrium growth of Ag-Al alloys tends to Ag-rich phases. Specifically, we have made incident a beam of Ag nanoclusters of size 4 nm on pure Al substrates for 5 mins and 15 mins and have studied the irradiated samples with X-ray Photoelectron Spectroscopy, Secondary Ion Mass Spectroscopy, and X-ray Diffraction. We have found that even at an overall presence of less than 0.1% of Ag atoms, the supersaturated Ag\(_{0.3}\)Al\(_{0.7}\) is formed with an fcc structure at ambient temperature with a better crystallinity than the host Al lattice. We have put forward an explanation based on the known low density and localized bonding electron structure of Al. We suggest that the results indicate a local stabilization of the lattice under the specific non-equilibrium condition which, on one hand, has the potential to grow new alloys with prescribed properties and on the other to the understanding of the Ag-Al bond in the Al-rich phases during transition from alloys to bimetallic compounds. These results create the motivation to study Ag-Al bonding, especially under non-equilibrium conditions, more extensively and intensively, using in particular X-ray Absorption Fine Structure Spectroscopy and this underway.

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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations. The data also forms part of an on-going study.

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