The Analysis of Coatings Produced by Accelerated Nanoparticles

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ABSTRACT

This paper investigates the form and structure of coatings formed by the deposition of accelerated elemental and alloy nanoparticles. The nanoparticles are formed by a 'terminated gas condensation' technique. The nanoparticles are produced by magnetron sputtering followed by thermalization and condensation in high pressure zones. The nanoparticles formed in this environment are further refined through a series of apertures and differentially pumped zones until the refined beam is passed on to the high vacuum sample chamber, hence 'terminated gas condensation'. The nanoparticles generated are negatively charged and may therefore be mass selected by a linear quadrupole and accelerated towards a substrate to form a surface coating or film. These coatings are of interest for a great many applications such as catalytic studies of soft landed nanoparticles, gas sensors, electronic materials on plastics as well as many more. The resulting films have been analysed by a variety of techniques including mass spectroscopy, SEM & TEM.

***Keywords*:** nanoparticle, deposition, catalysis, medicine

1 INTRODUCTION

Nanoparticles (NPS) have been synthetically produced by different techniques for many years. There are two main ways to produce NPS; by chemical synthesis, or by physical vapour condensation techniques. The approach described in this paper is a 'terminated gas condensation' technique. This technique has been studied by other researchers and is becoming of interest for many possible applications [1]. NPS are generated by DC magnetron sputtering followed by gas phase condensation. The resulting NPS tend to possess one excess electron. This excess electron allows the NPS to be electrostatically manipulated. The NPS may be accelerated towards a substrate to produce a wide variety of coating morphologies from nanoparticle powder, through porous films to crystalline structures. A linear quadrupole may be used to measure the mass distribution, or to act as a mass filter. Coatings produced by this technique form functional nanoparticle coatings, the structure and stoichiometry can be controlled to a high degree. One of the key advantages of this technique is that the kinetic energy of the impinging material can be controlled. The process is effectively non-thermal so that delicate plastics and organics may also be coated. Typically nanoparticles of diameter 5nm carry in the order of tens of thousands of atoms; with one excess electron surface charging is virtually eliminated. This paper describes some experiments which have been designed to characterise the source itself and some of the interesting materials produced. There are many possible application areas for this deposition technology. The materials of interest appear to fall into two categories; functional isolated NPS and functional films produced by the deposition of NPS. An obvious example of the former is catalysis where it is ideal to be able to produce a nanoparticle which is pure, of an exact size, and may be soft landed onto a surface whilst preserving its structural integrity. An example of a functional film might be a biosensor where a porous film of NPS is deposited to provide a massive surface area. There are also many possibilities in the area of functional medical coating and NPS.

The next generation of functional semiconductors will incorporate ordered nanoparticle alloys which will take advantage of the synthetically designed periodicity as well as the localised functionality of the individual nanoparticle. These materials are known as metamaterials [2].

2 EXPERIMENTAL

NPS are produced by a 'terminated gas condensation' technique. Figure one is a schematic diagram illustrating the principle of operation.

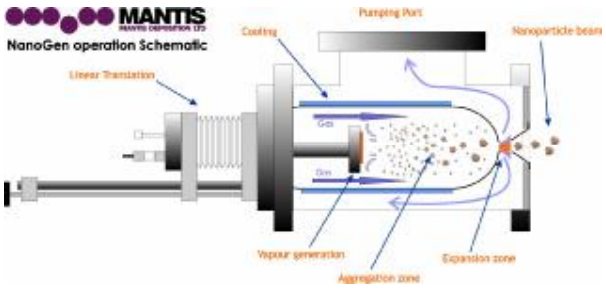

Figure 1: Nanoparticle source schematic.

A DC magnetron is used to sputter the source material target. The pressure in the aggregation zone is around 1 x 10^{-1} mbar. At this pressure the mean free path of the sputtered atoms is very small and thermalization occurs quickly. NPS are

formed as the sputtered material migrates to the first expansion zone. The size of the NPS is affected by several different parameters. The magnetron head can be moved within the aggregation zone. Reducing the distance from the magnetron head to the first expansion aperture reduces the distance and time whereby condensation can occur so the average particle size is reduced. The source allows introduction of helium carrier gas. Increasing the flow rate of helium reduces the average particle size by reducing the associated residence time in the aggregation zone. The DC magnetron is operated under a negative bias and it is observed that the NPS produced by this method tend to possess one additional electronic charge. After the first expansion aperture the NPS enter the differential pumping zone. Here most of the sputter and carrier gases are pumped away and the NPS supersonically expand to allow a narrower mass distribution to pass through the final expansion aperture. The pressure in the differential pumping zone tends to be around 1 x 10^{-3} mbar and the pressure in the sample chamber is typically around 5 x 10^{-5} mbar.

3 RESULTS

Because the generated NPS possess an excess electronic charge they may be electrostatically manipulated. It is possible to introduce mass spectrum measurement and mass filtering by using a linear quadrupole. The quadrupole does not require an ioniser as the NPS are already charged. Figure two is an example of a mass spectrum of copper clusters as measured by the quadrupole.

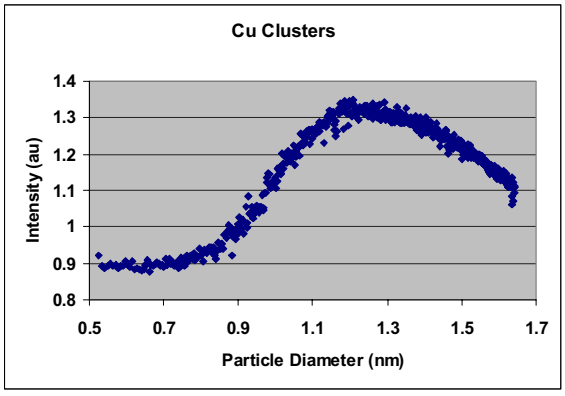

Figure 2 : Mass spectrum of copper NPS.

Typically NPS may be generated and measured with diameters ranging from ~0.7nm to 20nm in diameter. If the quadrupole is not inline then the particle diameter distribution is around +/- 20%. If the quadrupole is inline then the distribution can be reduced to around +/-2%.

If the substrate is positively biased then the NPS can be accelerated. If no bias is present at the substrate then the NPS are 'soft-landed' and retain their original structure. If the NPS are accelerated then they begin to adhere more strongly to the surface. As the kinetic energy of the NPS increases they begin to disassociate on the surface until finally they revert to a classical homogeneous material. Soft-landed NPS form a dark loosely bound powder. This powder may be collected and suspended in a solvent. At a range of around 300V to 4kV the NPS form an adherent coating where the density of the material is controlled by the accelerating voltage. The optical and electronic properties of these coatings have not yet been investigated. For example it is possible to produce a coating of pure copper which is red in colour and has a high electrical resistivity. Figure three illustrates three separate coatings of copper on gallium arsenide.

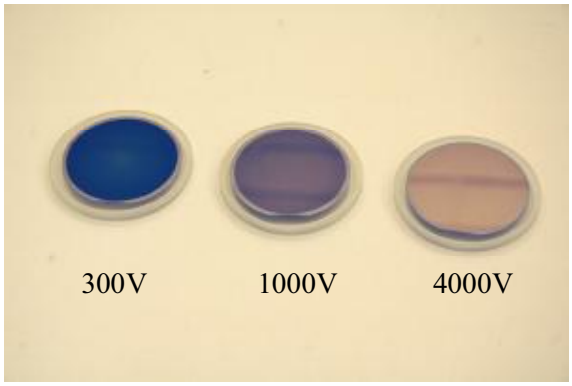

Figure 3 : Accelerated copper NPS on GaAs.

All of the films were deposited for the same period of time and under identical conditions, except that the bias applied to the gallium arsenide substrate was varied. The left hand side coating is a blue coloured copper film the accelerating bias was 300V, this coating is electrically insulating and mechanically unstable. The centre coating was produced using 1000V accelerating potential. It is dark brown in colour and has an in-plane resistance in the order of kOhms. This film is mechanically stable and cannot be removed using solvents. The right hand film (4000V) has been converted back to a metallic copper film; this film is highly adherent and conductive. If the accelerating potential is increased above 4000V then the copper film actually becomes silver indicating intermixing with the GaAs substrate. All of these coatings can be produced on a wide variety of substrates including insulators and plastics.

Figure four is a non-accelerated coating of titanium nitride. Oxide, nitride and hydride NPS may be produced by a variety of methods. If one of these gases is introduced to the sputter gas (typically argon) then it is possible to form the alloy during the sputter process. It is possible to control the mole fraction (and thus physical properties of the material) of the additional element by control of the partial pressure. It is also possible to oxidise metallic clusters by using an atomic beam.

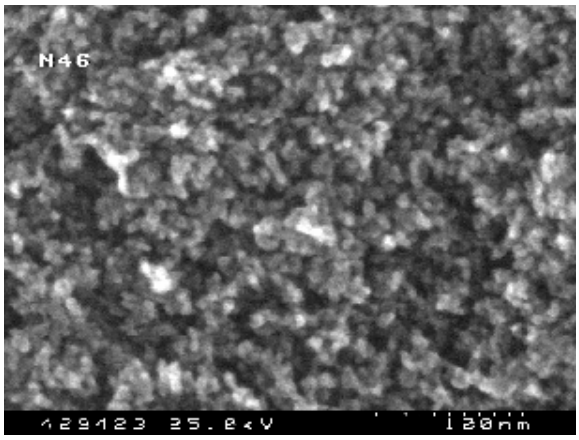

Figure 4 : A non-accelerated coating of TiN clusters

Figure five is a scanning electron microscope image of gold iridium NPS. The diameter is around 7-8nm. The average deposition rate for these samples is around 5nm/min.

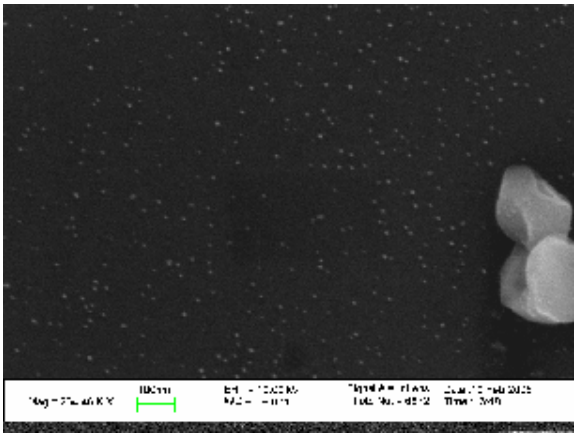

Figure 5 : SEM image of individual Au/Ir NPS.

These NPS were soft landed without using an accelerating voltage. Further investigation is underway to determine the exact size distribution and shape of these NPS.

Figures six and seven show TEM pictures of metal clusters deposited onto carbon coated grids. These samples were deposited under identical conditions except for the time of deposition, five minutes and forty seconds respectively. In this case the quadrupole was not used as an in-line mass filter and some variation in cluster diameter is observed.

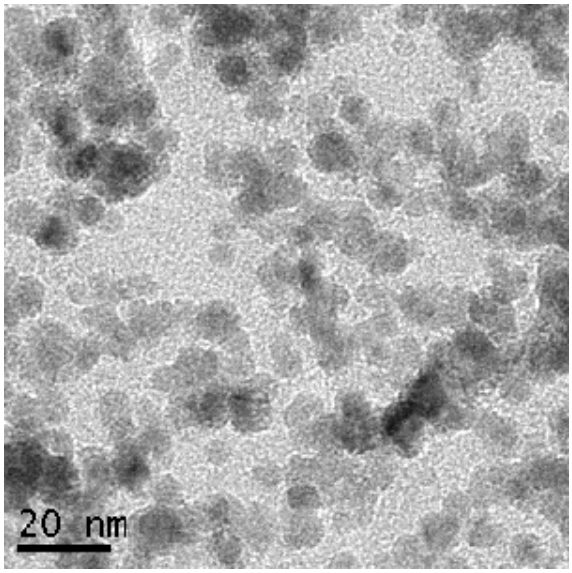

Figure 6 : Soft landed metallic NPS (5mins.).

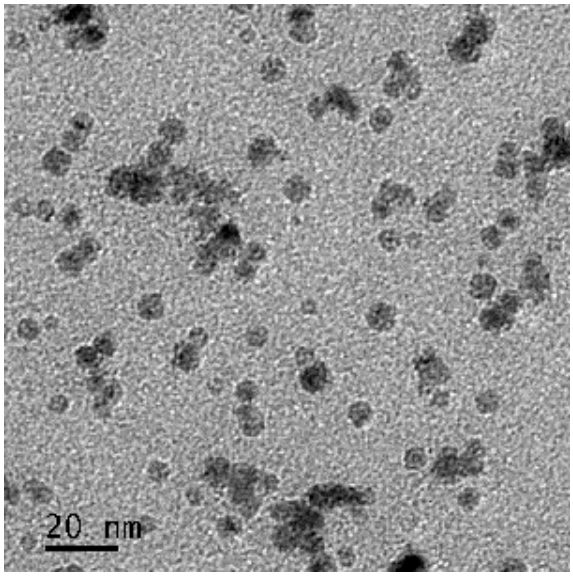

Figure 7 : Soft landed metallic NPS, (40s).

Figure eight is a high angle annular dark field image (HAADF) of a light coating of ruthenium NPS. The bright spots at the centre are ruthenium whilst the lighter areas indicate an oxide coating. These nanoparticles were deposited using 200v acceleration onto TEM grids. The NPS have oxidised on exposure to air. It is planned to encapsulate these NPS in the next set of experiments to avoid this oxidation. Encapsulation may be achieved by another accelerated nanoparticle film, or by a pure metallic coating.

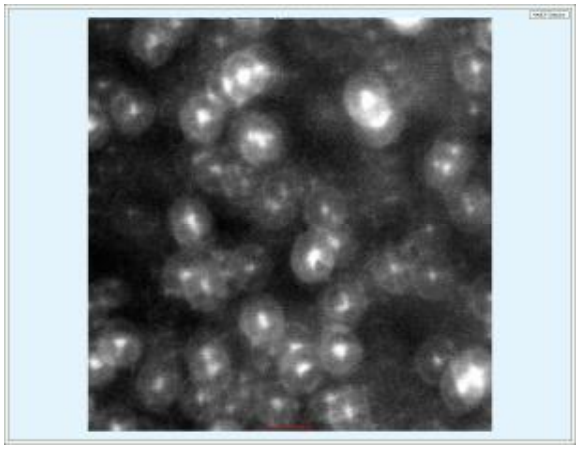

Figure 8 : Oxidised ruthenium NPS.

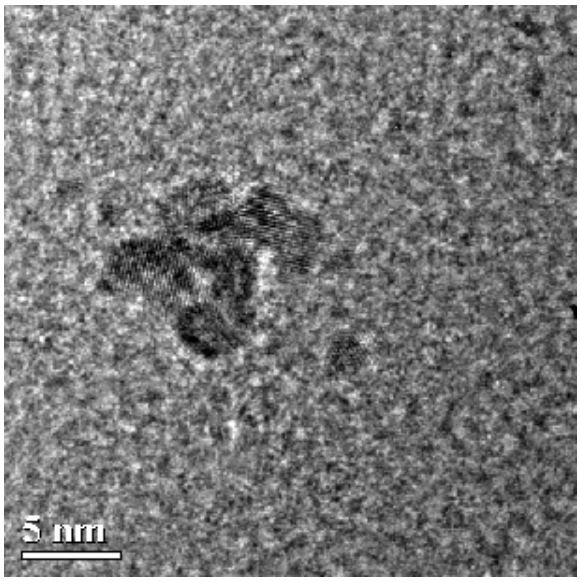

Figure 9 : High resolution TEM image of Ru NPS.

Figure nine is a high resolution TEM image of soft landed ruthenium NPS. Careful examination reveals crystalline atomic structure within the NPS. The integrity of this crystallinity will be affected by the accelerating voltage applied to the NPS and by the interaction of the NPS with surface bonds.

4 CONCLUSIONS

Nanoparticles have been produced using a 'terminated gas condensation' technique. It is possible to generate NPS of many different materials including alloys. The NPS generated possess one excess electronic charge and may therefore be electrostatically manipulated. Mass spectra of the nanoparticle beam have been obtained. Two main types of deposition have been studied; coatings whereby the NPS are accelerated towards a substrate to form functional materials and soft landed isolated clusters which, in the future, will allow the study of the physical and chemical properties of such materials.

5 FUTURE WORK

Future work will focus on several different areas. We plan to increase the amount of in-house development on the nanoparticle source as well as material deposition and application. This will allow the design of the nanoparticle source to evolve. The generation of NPS is an extremely complicated process unlike any other technique such as thermal evaporation or sputtering. Mantis is already working with both academic and industrial partners to progress this technology rapidly. The benefits of a refined process are the resulting materials which possess such unusual behaviour.

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G.Y.Chen. ATI, The University of Surrey, UK. (figures

Rotimi Ojifinni. The University of Texas, USA.

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