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Probing of unembedded metallic quantum dots with positrons

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Abstract. We employed the two detector coincident Doppler Broadening Technique (coPAS) to investigate Ag, Au and Ag/Au alloy quantum dots of varying sizes which were deposited in thin layers on glass slides. The Ag quantum dots range from 2 to 3 nm in diameter, while the Ag/Au alloy quantum dots exhibit Ag cores of 2 nm and 3 nm and Au shells of varying thickness. We investigate the possibility of positron confinement in the Ag core due to positron affinity differences between Ag and Au. We describe the results and their significance to resolving the issue of whether positrons annihilate within the quantum dot itself or whether surface and positron escape effects play an important role.

Introduction

The current intense technological interest in metal and semiconductor nanoclusters calls for a detailed understanding of their structural/electronic characteristics, of significance to their unique technological properties [1]. Positron annihilation spectroscopy has proven itself as a useful tool in the investigation of the electronic and structural properties of nanostructures. The research has concentrated predominantly on embedded nanostructures, where affinity differences between the host and the nanostructures induces confinement within the latter. This has led to highlights such as the mapping of the Fermi surface of Cu nanoclusters embedded in a Fe matrix [2]. As successful as this approach may be, it does not allow for complete freedom of choice in the compositon and size of the quantum dots to be investigated. An alternative method would be to deposit nanostructures of chosen size/composition on a substrate and profile them with a low energy positron beam. Promising advances have been made in this direction [3]. Here we investigate a series of metallic nanostructures, of varying composition and size and show that Ag's greater affinity (-5.36 eV for bulk Ag) does not lead to confinement of the positron in an Ag quantum dot with an Au (-4.59 eV for bulk Au) shell. We find a useful indicator of the amount of Au or Ag which is profiled by the positron and observe surface termination effects on the annihilation properties of the positron in otherwise similar quantum dots.

Experimental

The samples were prepared using inverse micelles [4]. Following chemical reduction of the metal ions, the surface was passivated by dodecanethiol, which is a strongly binding surfactant. The nanostructures measured were 2 nm Ag and with 0.5 nm Au shell, 3 nm Ag and with 0.1 nm, 0.3 nm, 1 nm and 2nm Au shells and 2 nm and 6-8 nm Au. All samples, except for the 6nm Au sample and the 2nm Ag covered with 0.5 nm Au were shipped in powder form. The powders were dissolved in Toluene ($C_6H_5C_3$) and deposited in thin layers on glass slides. Samples were profiled as a function of implantation energy. For each deposit the energy at which the positrons annihilate within the deposit (typically 1 keV) was chosen as the energy at which to run the coPAS studies. We also ran coPAS measurements on annealed Ag and Au foils as well as Si samples in order to be able to compute ratio spectra.

Results

Figures 1a and 1b show the ratio spectra to Si (in order to remove resolution effects) of the quantum dot samples together with those of the annealed Ag and Au foils, obtained by coPAS measurements. The two figures illustrate that the deposits can be divided into two groups.

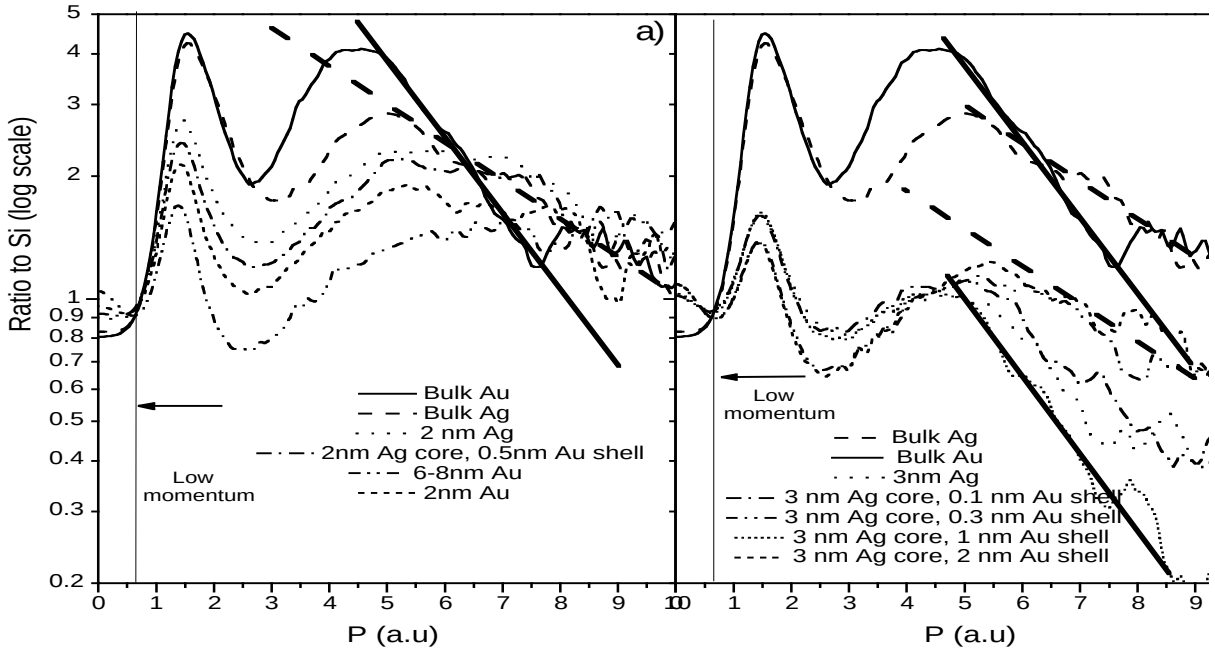

Figure 1) Ratio spectra of deposits to Si; on a log scale for better rendering of curve shape. Solid and dashed straight lines denote high momentum (> 5a.u.) behavior of Au and Ag bulk ratio curves. Dashed and solid straight lines in fig. 1b) are parallel.

The straight lines show the gradients of the high momentum components for Au and Ag. The samples in figure 1b) exhibit clear Ag and Au signs in the high momentum (> 5 a.u.)

tails, however, they do not correlate with the sample composition. The samples with 0.3 and 1 nm Au shell show the greatest Ag contribution, while the naked and 0.1 nm Au shell sample show a greater Au contribution. In figure 1a there appears to be no clear sign of an Ag or Au contribution. The reasons for this are not clear, however surface termination may have a profound effect on the quantum dot electronic structure [5], and are expected to modify the high momentum tails of the ratio curves. Note also the greater intensity of the low momentum (< 0.8 a.u.) components for the deposits as compared to the bulk Ag or Au. This may be due to surface effects on the quantum dot electronic structure or other possibilities such as Ag/Au interface defects, internal defects, or remnants of the solution they were deposited in.

In figure 2 we show the position of the centroid fitted to the ratio peak at approximately 1.5 a.u. The result is striking with a clear correlation between centroid position and composition of the sample.

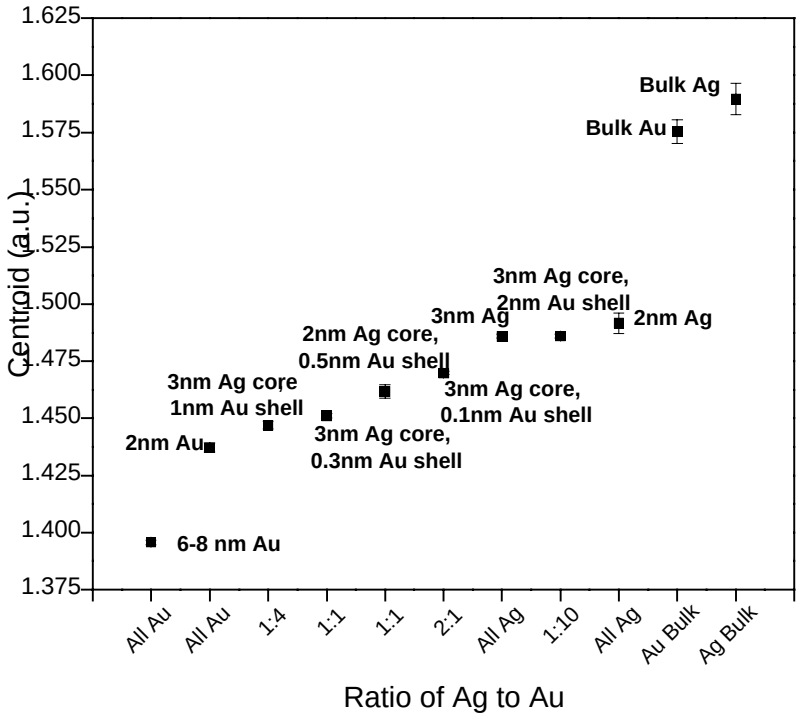

Figure 2. Plot of centroid of the peak of the ratio curve near 1.5 a.u. for all the samples measured.

The centroid for bulk Ag is greater than that for Au and as the amount of Au in the nanostructures decreases, the centroid increases. The sample AgAu46 appears to be the outlier. It is clear that we do not have confinement of the positron within the Ag core. Whether this is due to the positron being not thermalized or scattering off quantum dots,

being implanted in the shell, is not clear, and it would be interesting to have calculations to compare to.

In conclusion, we have observed surface induced changes in the high momentum annihilation signature of otherwise similar nanostructures. In addition, we find the position of the centroid of the first ratio peak in the ratio curves to Si to give us a measure of the amount of Au profiled by the positron. The affinity differences between Ag and Au are not sufficient to confine the positron within the Ag core..

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