DOI: 10.1017/S1431927603441366
Microsc Microanal 9(Suppl 2), 2003

Au Nanoparticles Formed in TiO_2 by Patterned Ion Implantation

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Ion implantation has been widely used for synthesis of metallic nanoparticles in oxide substrates through solid-state reaction due to their potential applications in nonlinear optical devices [1]. The obtainable of the nanoparticles with controlled size and distribution is very important for such applications. The size and depth distributions of metal nanoparticles in nanocomposite systems formed by "conventional" ion implantation tend to be fairly broad (only low-energy ion implantations at energies lower than 100 keV have been successfully used in synthesis of narrow depth arrays nanocrystals in oxide substrates [2]). That is a major obstacle to overcome for optimizing the characteristics of ion-implanted nanocomposites. To control the two-dimensional (2D) lateral arrays of nanoparticles, focus beam ion implantation (FIB) and "patterned" ion implantation may be the choice. Since Ga is currently the only source available in FIB, the application of FIB is limited.

In the present study, single-crystal TiO_2 that "patterned" implanted with Au ions through various masks were studied by analytically electron microscopy (AEM). The Au ion energy was 240 keV and ion fluence varied from low 10^{15} to 10^{17} ions/cm^2. X-ray energy-dispersive spectroscopy (EDS) mapping of Au with a SEM indicates that a 2D periodic arrays of micron sized Au rich dots is formed (Figure 1a). Plan-view high-angle annular dark-field (HAADF) image [3] revealed that these dots consist of Au nanoparticles (Figure 1b). Cross-sectional HAADF images taken from the sample showed that the Au nanoparticles have a single-band depth distribution (Figure 1c) and a relatively small size distribution (2-6 nm) compared with those formed in TiO_2 implanted with Au by conventional method (1-12 nm in size distribution). The Au nanopartciles in the conventionally implanted sample have a Gaussian depth distribution (~100 nm). High-resolution electron microscopy (HREM) image indicates that the Au nanoparticles lying in a single band near the surface of the substrate are surrounded by amorpherized substrate (Figure 1d).

To understand the formation mechanism of the single-band arrays of Au nanoparticles, we performed a series of patterned implantations at a same energy, 240 keV) and different doses (1×10^{15}/cm^2, 2×10^{15}/cm^2, 3×10^{15}/cm^2, and 5×10^{15}/cm^2) through a same size of masks (60×60nm). Instead of single-band arrays of Au nanoparticles, wave-like depth distributions were obtained from the as-implanted samples (Figure 2a and 2b). From the images, we can see that the Au nanoparticles have not been well developed in the as-implanted samples. After annealing at 1000K for 30 minutes in air, the Au nanoparticles have grown larger and still keep their wave-like depth distribution. This indicates that the mask itself cannot determine the depth distribution of the formed nanoparticles alone. It may be a combination effect of implantation parameters and mask size. Nevertheless, the present results clearly demonstrated that by patterned ion implantation, it is possible to obtain single-band arrays of Au nanoparticles in TiO_2.

References

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[4] The authors would like to thank S. Massing and A. Beck for performing the ion implantation. The JEOL-2010F STEM/TEM AEM used in this study was funded by NSF through the Grant DMR-9871177 and is operated by the EMAL at University of Michigan.

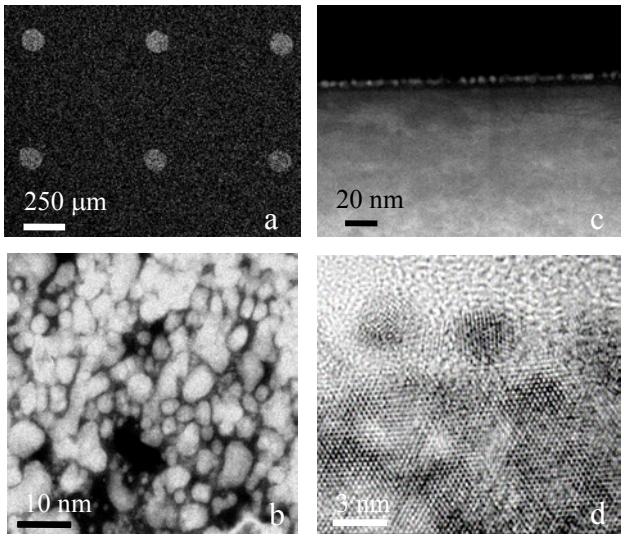

FIG. 1. (a) Plan-view EDS Au map of the sample with patterned implantation performed through a mask with large holes at an energy of 240 keV with a dose of $1\times10^{17}/cm^2$; (b) and (c) are plan-view and cross-sectional HAADF images of the same, respectively; (d) is a cross-sectional HREM image of the sample.

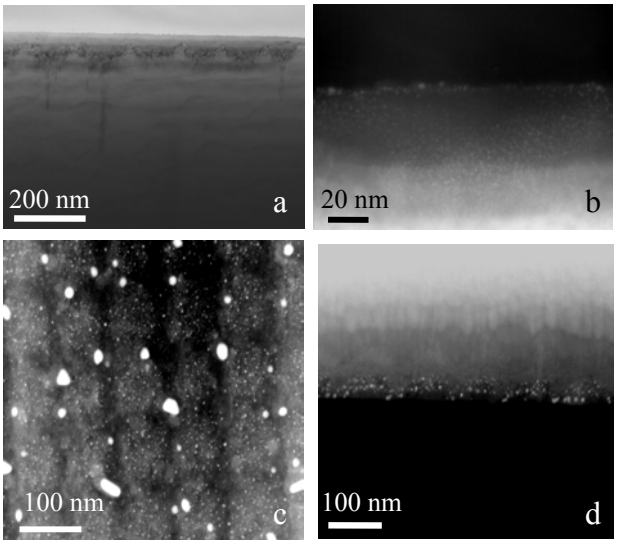

FIG. 2. Cross-sectional BF (a) and HAADF (b) images taken from the Au patterned implanted sample at 240 eV and a dose of $5\times10^{15}/cm^2$; (c) and (d) are plan-view and cross-sectional HAADF images taken from the sample with Au patterned implanted at 240 eV and a dose of $3\times10^{15}/cm^2$ (anneal at 1000K for 30 minutes in air), respectively.

https://doi.org/10.1017/S1431927603441366 Published online by Cambridge University Press