Sub-5 nm gold dot formation using retarding-field single ion deposition

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Gold dots of 2.5 nm mean diameter and 0.8 nm standard deviation have been fabricated successfully on chromium oxide (CrO_x) thin films. The CrO_x thin films were deposited on Si substrates by sputtering and gold dots were subsequently deposited by a retarding-field single ion deposition (RSID) technique. The formation of gold dots has been investigated systematically with landing energies from 100 to 900 eV and doses from 10 to 40 C/m^2. The dot diameter and density could be controlled by varying the landing energy and dose of gold ions arriving on the surface. The formation of single electron devices, quantum dots, nanopillars, and other nanoscale device structures is proposed using the RSID technique. © *1998 American Institute of Physics.* [S0003-6951(98)03748-6]

Nanostructure formation is expected to play an important role in future devices such as quantum dot devices, lateral resonant tunneling devices, single electron devices, nanopillars, and nanoemitters. The formation of the extremely small structures with high densities required in such devices is beyond the capability of conventional lithography techniques. Self-assembling processes have been proposed as alternative means of overcoming this limitation. Recently, the use of nanoscale metal and semiconductor particles for the formation of nanostructures has evolved rapidly. The deposition of colloidal particles was successfully employed in the fabrication of nanoscale structures for single electron devices[1–3] and Si nanoscale pillars for optical quantum devices have been formed by dry etching with a nanostructure mask of colloidal particles.[4]

A focused ion beam deposition technique with a retarding field is a new technique for forming nanoscale microstructures of various materials at selected positions on substrates. Recently, this technique has been successfully applied to the deposition of nanoscale islands needed for single electron devices.[5–7] However, in order to utilize this technique for such devices, nanostructures below 10 nm in diameter must be made and control over size distribution and density of dots is very important. The formation of islands is influenced by nucleation and surface mobility of single ions landing on the surface of substrates used. Therefore, the ion landing energy and ion dose together with a combination of the kinds of ions used and substrate material are key parameters for determining the size and density of islands. To achieve size reduction with a narrow size distribution, it is necessary to investigate the formation process of islands with energy and dose of ions landing on the surface varied over a wide range of values.

We report here the formation of gold islands on chromium oxide (CrO_x) films with our retarded field single ion deposition system (RSID) which has well controlled landing energy and dose. This technique enables us to investigate systematically the fabrication of sub-5 nm mean diameter nanodots and to control their size and density precisely.

A detailed description of the RSID system employed in this study is available elsewhere.[3] Gold ions were selected from an Au–Si–Be alloy liquid ion source by a magnetic separator. The column was operated at 20 kV and the sample potential was raised close to the beam accelerating voltage. The retarding field enabled us to control the landing energies of gold ions from 100 to ~900 eV. Ion doses incident on the substrate were varied from 10 to 40 C/m^2. All depositions were performed at room temperature.

CrO_x films were sputtered on a Si (100) substrate at room temperature by reactive gas sputtering of a Cr target with radio frequency (rf) power of 50 W, argon flow rate of 3 sscm, O_2 flow rate of 1 sscm, and at a pressure of 7×10^{-2} Pa. Under these conditions the CrO_x deposition rate was 1.8 nm/min. A thickness of 5 nm was used for the focused ion beam (FIB) depositions. X-ray photoelectron spectroscopy (XPS) analysis of the films showed clear peaks of Cr_2p_3 and Cr_2p_1 spectra attributed to 577.0 and 586.7 eV, respectively, which correspond to the typical spectra of Cr_2O_3. The surface morphology of CrO_x (2 nm)/Cr (5 nm) films on the Si substrate was evaluated by scanning tunneling microscopy (STM) and the root mean square of surface roughness of the films was around 1 nm. It was found that the sputter deposited CrO_x had a very smooth surface and there were no obvious structures corresponding to steps and terraces. The resistivity of the film was measured to be 2×10^5 Ω cm.

The CrO_x coated substrates were loaded in the RSID machine and a series of Au^+ depositions were performed varying the ion energies and dose. The resultant structures were observed with a field emission scanning electron microscope, with a resolution of ~0.8 nm. Figure 1 shows the evaluated mean diameter of gold islands. The mean diameter decreases rapidly with incident ion energies up to 400 eV, remains roughly constant up to 600 eV and then increases above 600 eV. At energies below 400 eV, the mean diameter increases considerably with increasing dose. The minimum

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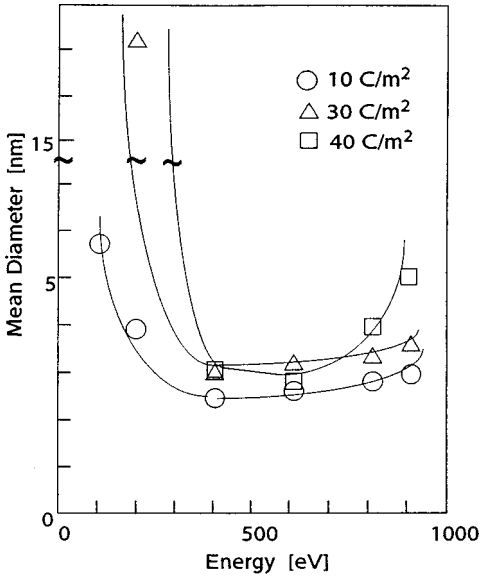

FIG. 1. Mean diameter of gold dots as a function of energy for doses of 10, 30, and 40 C/m^2.

value of mean diameter of gold islands obtained at 400 eV and 10 C/m^2 is estimated to be 2.5 nm. The standard deviations of diameters were 1.4, 0.8, and 0.7 nm at 100, 400, and 900 eV, respectively, with a dose of 10 C/m^2. The mean diameter and standard deviation tend to increase with an increasing dose. Figure 2 shows the dose dependence of dot density as a function of energy. The dot density of gold islands is roughly inversely proportional to the mean diameter. Assuming that dots of 2.5 nm mean diameter, obtained at 400 eV and 10 C/m^2, are uniformly distributed, the gaps between gold dots are estimated to be around 1.7 nm.

Figure 3 shows the scanning electron microscopy (SEM) images for four conditions. Figure 3(a) shows the dots for the lowest energy where the dots are randomly distributed. It is of interest to note that a few tens of dots are aligned closely linking with each other in some places as observed in Figs. 3(b) and 3(c). This is similar to results reported where Ag clusters deposited by a cluster source aggregated at steps on a graphite surface.[8] These facts indicate the possibility of developing self-alignment processes in dot formation using RSID although at present we cannot offer a relation between

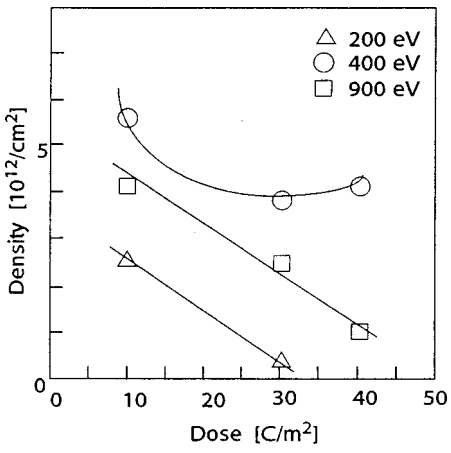

FIG. 2. Density of gold dots as a function of dose for energies of 200, 400, and 900 eV.

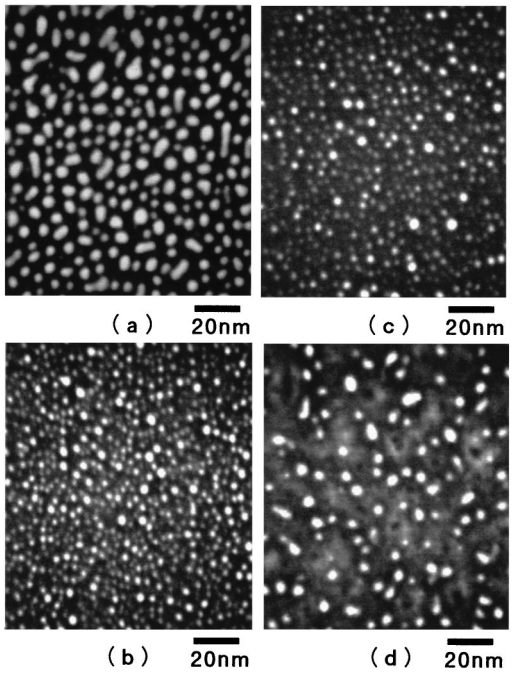

FIG. 3. Scanning electron microscope (SEM) micrographs of gold deposited on chromium oxide films at different conditions. The landing energy and dose are: (a) 100 eV and 10 C/m^2, (b) 400 eV and 10 C/m^2, (c) 900 eV and 10 C/m^2, and (d) 900 eV and 40 C/m^2.

dot alignment and initial surface morphology of CrO_x films. Furthermore, it is worth noting that some dark patches together with some light patches which are different from normal dot images, are observed for 900 eV and 40 C/m^2 deposition as shown in Fig. 3(d), while there were no such effects at 900 eV and 10 C/m^2 as shown in Fig. 3(c). We propose that the dark patches may be due to voids and the light ones due to an intermixed layer beneath the surface, caused by high energy ion impacts.

The formation mechanism of gold islands can be explained by a combination of ion beam induced nucleation, sputtering, and diffusion of gold atoms incident on the CrO_x surfaces. We consider that gold atoms on the surface which are struck by subsequent ions can break loose from their binding site and migrate randomly to seek local minima of the surface potential or an adjacent island. At a low energy of 200 eV, the range of Au^+ ions into Cr_2O_3 was estimated to be 1.9 nm by using a simple calculation.[9] The roughness of the surface is smaller than this depth and so the surface potential is relatively homogeneous. The atoms on the surface have a large surface mobility and so impacts on the near neighboring sites result in aggregation occurring randomly. Consequently, several ions coalesce into a large island. On the other hand, at energies above 200 eV, the sputtering effect becomes larger. Nagamichi[10] *et al.* measured the sticking probabilities of gold ions on gold films and observed a decrease with increasing gold ion energy.[10] The sticking probability is approximately unity at 50 eV, but decreases to 0.1 at 200 eV. At 400 eV, the calculated range of gold ions increases to 2.4 nm. The surface potential is modified due to the defects generated by ion impact and the ions incident on the surface become more pinned to their points of impact. Therefore, aggregation occurs at a local site due to the low surface mobility. Additionally, larger islands are sputtered by

ions arriving later and so island growth is reduced. At an energy of 900 eV, the projected range of Au^+ is 3.2 nm. The ions penetrate into the CrO_x films and cause intermixing and considerable defect formation. In fact, with increasing the dose at 900 eV landing energy, some voids on the surface and an intermixing layer inside the film were observed as shown in Fig. 3(d). The surface will be roughened at this energy and an aggregation will occur in the microhollow sites formed on the surface resulting in making the dot diameter larger.

In conclusion, we have investigated the formation of nanoscale gold islands on a CrO_x layer using the RSID technique, varying the ion landing energy and dose. It was found that precise control over the dot size and density was possible by selecting the landing energy and dose. Gold dots of mean diameter of 2.5 nm with standard deviation of 0.8 nm were formed at 400 eV and 10 C/m^2. This method is proposed as a novel process for fabricating sub-5 nm structures for single electron devices and nanopillars.

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