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NANOSTRUCTURED ARRAYS FORMED BY FINELY FOCUSED ION BEAMS

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ABSTRACT

Amorphous, polycrystalline, and single crystal nanometer dimension particles can be formed in a variety of substrates by ion implantation and subsequent annealing. Such composite colloidal materials exhibit unique optical properties that could be useful in optical devices, switches, and waveguides. However colloids formed by blanket implantation are not uniform in size due to the nonuniform density of the implant, resulting in diminution of the size dependent optical properties. The object of the present work is to form more uniform size particles arranged in a 2-dimensional lattice by using a finely focused ion beam to implant identical ion doses only into nanometer size regions located at each point of a rectangular lattice. Initial work is being done with a 30 keV Ga beam implanted into Si. Results of particle formation as a function of implant conditions as analyzed by Rutherford backscattering, x-ray analysis, atomic force microscopy, and both scanning and transmission electron microscopy will be presented and discussed.

INTRODUCTION

It has been shown that amorphous, polycrystalline, and single crystal nanoparticles can be formed in a variety of substrates by ion implantation under prescribed conditions combined with subsequent thermal annealing [1,2,3]. Typical sizes of these particles range from a few nanometers to several hundred nanometers in diameter. They may be metals or semiconductors and can be made of either single or multiple elements, including compound semiconductors, by using sequential implantation techniques. These composite materials frequently exhibit unique optical properties and may find applications in optical devices. One problem of composite materials formed in this way is that the particle size is generally not uniform. In addition, the particles are randomly distributed throughout the implanted region. The purpose of this work is to make uniformly spaced lattices of colloidal particles of more uniform size by using a finely focused ion beam (FEI, FIB200) to implant ions only into a microscopic region (typically 60 nm diameter) at each point of a two-dimensional array. Simulations using a kinetic lattice Monte Carlo code indicate that such localized implants should form a localized distribution of colloids that, under proper conditions, may Ostwald ripen into a single large colloid at each lattice site [4]. Under these ideal circumstances the colloids formed would be of nearly uniform size because of the identical particle dose implanted at each spot, and in addition they would be uniformly arranged on a two-dimensional lattice. Such a composite would exhibit greatly enhanced optical characteristics.

EXPERIMENT

Bulk implants of Ga and As into Si(100) at energies of 35 to 160 keV were used to study ion retention vs. dose and GaAs formation. They were made on an Extrion 200-1000 ion

implantation accelerator at different doses and substrate temperatures in order to understand the behavior of Ga and As during the low energy implantation which is typical of focused ion beam (FIB) formation of patterned samples. The FIB samples themselves were implanted at 30 keV and room temperature for a variety of different doses, dose rates, beam diameters, and spot patterns using an FEI FIB-2000 focused ion beam system. Substrate temperatures were not controlled during FIB processing.

A number of techniques were employed to study the completed FIB patterned samples. Rutherford backscattering (RBS) using He-4 at 2.3 MeV and a scattering angle of 160 degrees was used to determine the absolute amounts of Ga retained in the samples after processing. Scanning electron microscopy (SEM) on a JEOL 840 operating at 10 keV was used to observe the implanted pattern as well as the size and shape of the individual dots. Atomic Force Microscopy (AFM) with a digital Instruments Nanoscope III was effective in determining the geometry of the individual implanted dots, including the depth of holes and the height of raised dots, as well as the uniformity of the over all pattern. Low resolution TEM images were taken on a Philips EM400 operating at 100 keV, while high resolution images and EDS spectra were made on a Philips CM200 at 200 keV.

RESULTS AND DISCUSSION

Saturation Concentration

Since the FIB was limited to 30 keV, it was necessary to determine the sputtering coefficient for 30 keV Ga and, as a result, the saturation concentration of Ga that could be implanted at this energy. Book values for the sputter coefficient ranged around 2 [5]. We measured the retained saturation amount of Ga directly as a function of incident fluence for Ga on Si. These results are shown in Fig. 1, which includes values at different substrate temperatures, as well as values for As at the same energy, and a retention curve calculated with the analytical code Profile [6]. In order to fit the experimental Ga data at liquid nitrogen

Fig. 1 Retained vs. incident fluence for 35 keV Ga and As on Si measured by RBS at liquid nitrogen, room, and 300C temperatures. Also shown is a Profile Code calculation for a sputter coefficient of 2.8.

temperatures, a sputtering coefficient of 2.8 was required in Profile. This is close to the tabulated value assumed by Profile (3.1), and is the value that will be used in our discussions. Note that above room temperature, very little of the incident Ga is retained, due to evaporation from the surface, while at room temperature an interesting phenomenon occurs. It appears that significantly more Ga can be retained at room temperature than at LN₂. More careful

investigation of the RBS spectra reveals that this Ga is concentrated on the surface as evidenced by the shift of the Si edge to lower energy. It appears that for the room temperature samples, the Ga is sufficiently mobile to form a surface layer of near liquid (Ga melts at 29C) Ga globules that is less effectively sputtered by the incident Ga beam. These globules can be observed optically and are sufficiently "liquid" that they can be blown from the surface with air.

Low Energy Formation of GaAs by Blanket Implants

The next step was to determine whether GaAs could be formed in Si by ion implantation at energies as low as 30 keV as required by the FIB system. We had previously shown that crystalline GaAs could be formed during ion implantation of the individual elements at both 500 keV and 150 keV with subsequent thermal annealing,* but there were indications that proximity to the surface might result in loss of material rather than compound formation. To study this, Si(100) samples were implanted sequentially at 35 keV with 5×10^{16} each of Ga and As/cm² at 500C, both with As first, and with Ga first. As seen in the RBS spectra of Fig. 2a, most of the Ga is lost from samples in which the Ga is implanted first, so studies were concentrated on

Fig. 2a RBS spectra of 35 keV Ga + As, 5×10^{16} each in Si, as implanted, and annealed at 600C.

Fig. 2b RBS spectra of 35 keV As + Ga, 5×10^{16} each in Si, as implanted, and annealed at 600C.

samples implanted first with As and subsequently with Ga. Fig. 2b indicates that most of the Ga and As are retained when implanted in this order. Although similar samples implanted at 150 keV show clear x-ray evidence for the formation of crystalline GaAs, the samples implanted at FIB energies (35 keV) do not. Since formation of GaAs in blanket implanted samples had not been demonstrated, this work on FIB formation of colloids was directed initially toward the formation of elemental Ga particles.

Theoretical Simulation of FIB Implantation

Kinetic 3D lattice Monte-Carlo simulations are a suitable tool for modeling all basic physical processes of ion beam synthesis of nanocrystals.* For the simulations presented here, a kinetic Ising model is used to incorporate effective Ga-Ga interactions within a neutral matrix (Ga-Si interactions can thus be ignored). For a symmetric initial distribution of implanted ions, the code in general predicts aggregation into multiple colloids, with possible Ostwald ripening into single particles at each lattice site. Discussing the present physical parameters, it is obvious that no spherical single precipitates are to be expected. For a nominal beam diameter of 120 nm (FWHM) and a projected range of about 25 nm, at best a single disk should be formed because of the large lateral to vertical ratio of the effective deposition volume. For simplicity the

Fig. 3a Optical micrograph of 30 eV Ga 64x64 row pattern on Si. Doses vary from 2×10^{10} on the left to 1×10^6 on the right. Square is 1.1x1.1 mm.

Fig. 3b Optical micrograph of Ga dots on Si at 30 keV and 2×10^{10} Ga/dot (left side of Fig. 2a) Spacing between dots is 20 microns.

evolution of a single spot was studied starting with an idealized initial configuration matching the assumed Gaussian-like deposited Ga density used in this work. According to the preliminary MC simulation for this set of parameters, formation of a central disk-like nanocrystal is not clear.

Array Formation Using a 30 keV Ga Focused Ion Beam

The 30 keV Ga focused ion beam from the FIB-2000 was used to produce arrays of implanted spots at a variety of different doses. Nominal beam diameters of 60 and 120 nm and currents of 170 and 1000 pA, respectively, were used to form 1.1 mm square patterns of implanted spots in 2-dimensional rectangular lattices on Si substrates. In general, in spite of careful iterative focusing of the ion beam, the observed implant spots are far larger (200 x in area) and less symmetric than the nominal beam size. Optical micrographs of Fig. 3 show a grid of spots implanted with the 30 keV 120 nm beam at spacings of 20 microns between spots. Doses on this sample were increased by a factor of 4 after every 8 rows from a minimum of 1.25×10^6 to 2.05×10^{10} Ga/spot over the 64 row grid, so that a wide range of incident fluences

Fig. 4a AFM inverted micrograph of deep hole produced by 2×10^{10} Ga/spot at 30 keV (Region 1).

Fig. 4b AFM micrograph of raised dimple produced by 2×10^7 Ga/spot at 30 keV (Region 6).

Table I: Doses Based on AFM Measured Spot Areas

Region	Ions/Spot	Area cm ²	Dose Ions/cm ²	Topography
1	2.05E+10	2.85E-08	7.18E+17	Deep Hole (2 micron)
2	5.12E+09			Deep Hole
3	1.28E+09	1.24E-08	1.03E+17	Hole
4	3.20E+08			Hole
5	8.00E+07	1.12E-08	7.14E+15	Dimple with Hole
6	2.00E+07			Dimple
7	5.00E+06			Smear
8	1.25E+06			No Spots

would be present. The purpose of this sample was to determine, in light of the disparity between nominal and observed spot sizes, the most effective dose per area for colloid formation. The results in terms of ions/cm² of observed spot area and surface topography as measured by AFM are shown in table I. As shown in Fig. 4, the higher doses produce deep holes, the lightest doses leave the substrate unaffected, and intermediate doses produce a slight rise in the implanted region. The raised areas at moderate doses are presumed to be due to incorporation of Ga along with the conversion of the area from single crystal Si to the less dense amorphous phase. The high aspect ratio holes at high doses clearly represent a poor geometry from which to form the desired single uniform size colloid at each lattice site, while the lowest doses provide insufficient Ga to produce a colloid. Therefore, the moderate dose regions, such as region 5 in the table, with a dose of 7E15 ions/cm², should be most interesting.

The presence of Ga in the implanted dots has been observed by several techniques. Confirmation of the retention of Ga has been shown by RBS to be 1.1×10^{14} Ga/cm² over the entire pattern, which is in agreement with the amount expected to be retained after sputtering. The qualitative presence of Ga in each individual lattice spot has been demonstrated by x-ray analysis by scanning the pattern with a 1.5 micron white x-ray beam and observing the resulting Ga line, which is observed only when the beam is on a spot. Fig. 5 shows a TEM image of a particle of Ga formed near the edge of an implanted spot taken from region 4 in the table. The particle is about 18 nm in diameter and can be positively identified as Ga from the EDS spectrum in the figure. Therefore small Ga colloids are formed at the lattice points, but uniform single colloids have not yet been observed.

Fig. 5a TEM micrograph showing Moire fringes of Ga particle formed by 3.2×10^8 30 keV Ga/spot (Region 4).

Fig. 5b EDS spectrum from particle in 5a indicating that the particle is Ga.

CONCLUSION

It has been demonstrated that a 2-dimensional lattice of Ga dots can be written on a Si substrate using a programmed finely focused ion beam at 30 keV. Aggregation of the roughly Gaussian implanted profile into a single particle at each of the lattice sites has not been demonstrated, but it is clear that Ga is retained in the substrate and does form small crystalline colloids. The dose and energy, and thus the depth, of the implanted ions appears to be critical in the formation of larger single particles, since the Ga ions must be implanted into a relatively undisturbed region of the substrate in order to form a single colloid. High doses drill holes into the substrate surface (See Fig. 5), leaving Ga spread around the wall and bottom of the hole, which produces an unsuitable geometry from which to diffuse the Ga into a single particle. Therefore the fluence should be limited to a value which leaves the implanted regions of the surface relatively flat. Based on the current work, such doses are on the order of 1×10^{16} ions/cm². In addition, for the formation of compound semiconductors, the individual elements, Ga and As, must be buried deep enough beneath the surface so that they do not escape from the surface during annealing or even during the implant itself. To date, using a blanket implant of 35 keV As followed by localized 30 keV FIB implants of Ga, we have not been able to produce GaAs quantum dots, although we have demonstrated that GaAs nanoparticles can be formed by blanket sequential implantation of the individual elements at 150 keV. Several techniques are proposed to produce such compound semiconductor quantum dots by the FIB process in the future, including higher energy (150 keV) FIB, and capping of the pattern with SiO₂ prior to high temperature annealing to form the GaAs. These ideas are currently undergoing further study.

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