Development of Semiconductor Detectors for Fast Neutron Radiography

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Abstract
A high-energy neutron detector has been developed using a semiconductor diode fabricated from bulk gallium arsenide wafers with a polyethylene neutron converter layer. Typical thickness of the diode layer is 250 to 300 pm with bias voltages of 30 to 50 volts. Converter thicknesses up to 2030 pm have been tested. GaS neutron detectors offer many advantages over existing detectors including positional information, directional dependence, gamma discrimination, radiation hardness, and spectral tailoring.

Polyethylene-coated detectors have been shown to detect 14 MeV neutrons directly from a D-T neutron generator without interference from gamma rays or scattered neutrons. An array of small diode detectors can be assembled to perform fast neutron radiography with direct digital readout and real-time display of the image produced. In addition because the detectors are insensitive to gamma rays and low energy neutrons, highly radioactive samples (such as spent nuclear fuel or transuranic waste drums) could be radiographed.

INTRODUCTION
Neutron radiography is a well-developed and commercially viable technique that is used throughout the world for non-destructive examination. The technique employs a neutron source and collimators to produce a neutron beam. A sample is then placed in the neutron beam and recording media are placed directly behind the sample. The attenuation of the beam by the sample produces a two-dimensional "shadow image" of the sample. A more detailed description of neutron radiography can be found in the literature [12].

Thermal and epithermal neutron radiography are the most widely used forms of neutron radiography. These use low-energy neutrons which have a limited range in most materials of interest. Fast neutron radiography, i.e. utilizing neutrons with energies around 14 MeV produced from the D-T reaction, has been explored as a non-destructive examination tool for larger samples because of the greater penetrability of the neutrons [3-6]. The recording media at these energies has been almost exclusively proton-producing plastic coupled with X-ray scintillation screens. A sheet of light-sensitive film is placed in contact with the scintillation screens to record a latent image on the film. The film is then removed and chemically processed to produce a radiograph. This process has been shown to produce reasonable radiographs, but it has serious limitations. The technique is slow because of the time it takes to produce the image (exposure time) and the time it takes to develop the film. The technique is inconsistent because of the chemical processing. In addition, the processing requires specialized equipment and chemicals which introduce environmental and industrial hazards for use and disposal. The imaging screens and film are sensitive to gamma radiation and X-rays which means that the screens and film must be shielded (with some neutron 10SS) and samples cannot be radioactive. Another drawback is that the images produced are not digital. The radiograph must be scanned to produce a digital image with a loss in resolution and contrast due to limitations in scanning technology.

This paper discusses the development of a new type of coated semiconductor detector for the detection of fast neutrons. Small contacts are deposited on semi-insulating bulk gallium arsenide (GaAs) wafers and then coated with a hydrogen-rich material, e.g. polyethylene. A direct read-out of the detector count rate is obtained with standard electronics. This configuration allows multiple diodes to be created using a single wafer such that positional information...
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Nanocluster Formation During Ion Irradiation of SiO₂/Ag/SiO₂ Multilayers

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Abstract
Nanocluster formation during heavy ion bombardment of a thin contiguous Ag layer sandwiched between two continuous SiO₂ layers has been observed using in-situ TEM. During ion bombardment, irradiation-induced plastic flow of the Ag film enlarges pre-existing pin holes and separates the film at grain boundaries transforming the as-deposited thin Ag film into three-dimensional microcrystals having diameters greater than 30 nm. This plastic flow process is similar to that observed in free-standing Ag specimens during heavy ion irradiation. In addition to plastic flow, ballistic recoils inject Ag atoms into the SiO₂ where they precipitate into nanoclusters. Both effects are greatly enhanced by simultaneous electron and ion irradiation.

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Introduction

Composite systems formed of nanometer-sized metallic clusters embedded in dielectric matrices exhibit non-linear optical properties with many potential optoelectronic applications. Several methods have been used to synthesize these exotic systems [1-6], including high-temperature glass fusion, sputtering, sol-gel ion exchange, and ion implantation. It has been demonstrated [7-9] that ion-beam mixing of metal-SiO$_2$ multilayers could be used to create metallic clusters in an SiO$_2$ substrate over depths of a few micrometers. This ion-beam mixing process was previously studied by in situ Rutherford backscattering (RBS), and the final microstructure, consisting of large particles and nanoclusters formed by high dose irradiation, was characterized ex situ by optical absorption, x-ray diffraction and transmission electron microscopy (TEM) experiments [7-9].

Those authors concluded, using standard RBS analysis, that complete mixing between the Ag and SiO$_2$ was achieved. Optical absorption and transmission electron microscopy (TEM) indicated that nanometer size Ag particles were formed after the highest ion dose. An RBS spectrum is a one-dimensional convolution of ion energy loss in the direction normal to the specimen surface and, hence, is not sensitive to lateral compositional variations. The three-dimensional microstructural evolution reported in the present paper indicates that accurate deconvolution of the measured RBS spectrum is impracticable. Neither the nucleation of metal colloids nor the three-dimensional microstructure evolution could be obtained from the RBS measurements made during ion-beam mixing. In addition, the authors noted that the x-ray signal from the nanoparticles was overwhelmed by the signal from the contiguous metallic layer, precluding extraction of any information regarding the early stages of colloid formation [9]. The single TEM micrograph taken at the completion of the ion-beam mixing gave the false impression that formation of the large inclusions was due to lateral segregation.

In the present work, nanocluster formation is directly observed using in-situ TEM during ion bombardment of an SiO$_2$/Ag/SiO$_2$ multilayer. As detailed below, two independent mechanisms are involved in the conversion of the embedded Ag film into large and small particles.

Experimental

Samples were grown by electron-beam deposition of a 15-nm thick Ag layer on bulk SiO$_2$ followed by electron beam deposition of 150 nm of SiO$_2$ in a vacuum of 10$^{-7}$ mbar. TEM specimens were prepared by core-drilling 3 mm diameter disks, grinding the center of the disks from the bulk SiO$_2$ side to near perforation, then finally ion milling the bulk layer to perforation. The ion milling completely removed
the SiO$_2$ layer in the area directly adjacent to the perforation; however TEM observations were performed only in areas where all three layers were intact. Because of its much higher electron density, the TEM images primarily show the areas covered by Ag. Before ion irradiation the Ag layer was contiguous, but contained holes between individual crystal grains, as shown in Fig. 1a.

Observations were made in a Hitachi H-9000 transmission electron microscope operating at 300 kV located in the IVEM/Accelerator facility at Argonne National Laboratory [10]. In this facility, an ion beam line enters at 30° from the microscope's electron axis. The specimen was tilted 15° toward the ion beam so that both ions and electrons were incident on the specimen at 15° from the foil normal. Specimens were irradiated at room temperature with 400 keV Xe$^+$ ions at a dose-rate of $1.2 \times 10^{11}$ ions/cm$^2$/s. Images were recorded during interruptions of the ion irradiation in an area that was not otherwise electron irradiated. The ion range and damage production were estimated from full cascade calculations using the Monte-Carlo code TRIM [11]. A large fraction of the Xe ions stop in the Ag layer because of its higher atomic density. After the highest dose, the Xe concentration in the Ag approaches 5 at.%, and damage in the Ag approaches 90 displacements per atom.

**Results**

Changes occurring to the silver film following irradiation of the SiO$_2$/Ag/SiO$_2$ sandwich to successively higher doses of 400 keV Xe ions are illustrated in figure 1. The behavior under the ion beam is complex but can be divided into four different components which will be discussed separately below:

(i) enlargement of pre-existing holes and separation of grain boundaries in the film leading to a transformation from a contiguous film to (at the highest doses) isolated nearly spherical particles.

(ii) sporadic separation and migration of small pieces of the Ag film laterally from edges of the film into pre-existing holes. These pieces also transform into near-spherical particles 10 – 20 nm in diameter

(iii) dispersal of Ag from the film (and from detached pieces of film) into the SiO$_2$ leading to

(iv) nucleation of nanoclusters 2 – 3 nm in diameter
(i) Hole enlargement
The original 15 nm thick Ag film can be clearly seen to transform into a lace-like structure over the dose range exhibited in figure 1. Every hole in the final image is traceable to an initial hole or grain boundary. Inspection of figure 1d reveals that at this stage much of the film has been transformed into interconnected particles of silver. Observations over a range of specimen tilt angles at this dose showed little change in the projected dimensions of the individual particles with tilt, indicating that they were tending towards a spherical shape; the diameters of the particles at this stage ranging from 20 – 70 nm. The change to a near-spherical shape is consistent with the minimization of the interfacial energy of the individual Ag particles and the SiO₂ matrix; the surface tension (or surface free energy) of metals being greater than that of glasses [12]. The irradiation enables morphological changes to occur that otherwise would not be expected to occur at room temperature. The three-dimensional shape of the Ag particles renders techniques that laterally average over the specimen, such as RBS, extremely difficult to deconvolute and interpret.

The mechanism underlying these changes is irradiation-induced plastic flow. Plastic flow associated with individual ion impacts has been seen to lead to the formation of holes in thin Au foils [13] and craters in self-supporting thin films of a number of fcc metals, including Au [14] and Ag [15]. The plastic flow process occurs in a free-standing Ag film or a Ag film sandwiched between SiO₂ layers. Plastic flow in free-standing specimens results a thickening and a balling up of the edges. The response of the sandwiched Ag film is modified by the geometric constraints. Plastic flow of the silver might be expected to occur less readily at the Ag/SiO₂ interface than at an Ag/vacuum interface because of a reduced interfacial energy. However, it should be noted that amorphous SiO₂ also undergoes plastic flow during heavy ion irradiation [16]. Clearly, flow must occur in both materials for the observed transformation to occur without delamination of the multilayer structure (which is not observed).

The fractional coverage of the Ag film, initially 95% (averaged over an area approximately ten times that shown in figure 1), reduced exponentially with ion dose to 58% after irradiation to $1.5 \times 10^{16}$ ions/cm². This coverage corresponds to spherical particles with their surfaces separated by a distance equal to 1/3 the particle radius. For an initial film thickness of 15 nm, conservation of Ag yields particles with a diameter of about 40 nm, a value that is at the middle of the particle size range present in figure 1d. The shape change is due to pulsed localized flow controlled by surface tension forces that act upon small regions momentarily melted by individual ion impacts. The localized flow eventually transforms the thin film into nearly spherical microcrystals.
Figure 2 shows an area of the sandwich structure after the highest dose used in the current experiments, $1.5 \times 10^{16}$ ions/cm$^2$. It is difficult to distinguish between the microparticles resulting from balling of the original film and the nanoclusters that have formed from dispersed Ag. Continued irradiation has dispersed Ag from the microparticles into nanoclusters resulting in a narrowing of the size distribution of the Ag particles. This is discussed in part iii.

(ii) Migration of small pieces of the Ag film
Of the four observed processes, this is the one that is least well understood. Inspection of figure 1a) and 1b) shows that after a dose of $10^{14}$ ions/cm$^2$, small pieces of film have detached themselves and moved laterally towards the center of the hole. Under continued irradiation these film segments transform into spherical particles by plastic flow. It seems unlikely that such a lateral migration of parts of the Ag film could occur (at such a low dose) as a result of displacement effects due to the ion irradiation. The mechanism responsible for this movement is unknown. We speculate that this process may result from Coulomb forces due to charging, or ion and electron induced excitation processes in the SiO$_2$.

(iii) Dispersal of Ag into the SiO$_2$
At the same time that the above processes are occurring, Ag from both the contiguous film and from the detached segments (and later from the isolated spherical particles) is being dispersed into the SiO$_2$ matrix. The dispersed Ag can be seen in the micrographs (due to mass thickness effects) as a 'shadow' around the edges of the retreating film. Calculations using the Monte-Carlo code TRIM [11] indicate that, after the highest dose shown in figure 1, approximately 10% of the Ag is expected to be ballistically mixed into the SiO$_2$. The calculated Ag concentration decreases monotonically from the interface with the median at about 10 nm from the interface. Radiation enhanced diffusion of Ag in SiO$_2$ may increase the width of the distribution of dispersed Ag [17,18]. The amount of ballistically implanted Ag will depend on the dose during which an area was covered by Ag. Although it was not possible to determine directly the quantity of dispersed Ag, a lower limit can be obtained by determining the amount of Ag contained in the nanoclusters that precipitate out from this dispersed Ag (see next section). These could only be clearly imaged in regions from which the Ag film had withdrawn due to plastic flow. A rough estimate leads to the conclusion that up to 3% of the Ag is contained in visible nanoclusters following a Xe dose of $10^{16}$ ions/cm$^2$. 
Nucleation of nanoclusters
Nanoclusters are observed most clearly in regions from which the film has retreated and can be clearly seen around the inside of the hole in figure 1d. Their density is highest nearer to the Ag film or microparticle which served as the source of ballistically implanted Ag. Stereo microscopy has revealed that the nanoclusters are distributed in depth, probably over a depth greater than that to be expected from considerations of simple ballistic mixing, although the precise depth over which they are distributed could not be determined. Measurement of the size of 75 nanoclusters following irradiation to a dose of $8 \times 10^{15}$ ions/cm$^2$ (in regions from which the Ag film has receded) reveals a mean diameter of 2.4 nm. Inspection reveals that nanoclusters also form in regions still covered by the Ag film.

Continued irradiation up to the highest dose used in the present experiments, $1.5 \times 10^{16}$ ions/cm$^2$, yields the morphology shown in figure 2. Note that the dose was limited to this value to avoid loss of the integrity of the multilayer structure due to sputtering of the top SiO$_2$ layer. RBS measurements after the in-situ TEM measurements revealed that approximately 100 nm of the original 150 nm SiO$_2$ layer was still in place at the end of the experiments. Figure 2 indicates clearly that, following conversion of the contiguous Ag film into microparticles, irradiation with Xe transferred silver from the microparticles to the nanoclusters thereby tending to narrow the cluster size distribution.

The precipitation of Ag into clusters, from the ballistically dispersed Ag, is similar to the behavior of other systems that precipitate from a background of insoluble material dispersed in a matrix, such as inert gases implanted into metals. In these systems, in which nanometer-sized clusters (bubbles) form, only a fraction of the implanted gas (10 –50%) is measured to be contained in the visible clusters. In the present work, up to an estimated $1/3$ of the dispersed Ag is in visible clusters.

Conclusions
We have followed the evolution, using in-situ TEM, a SiO$_2$/Ag/SiO$_2$ multilayer during irradiation with 400 keV Xe ions. The system evolves from an initial planar configuration into one in which the Ag is in spherical or near spherical particles dispersed in the SiO$_2$. The particle size distribution is bimodal with the larger component (approximately twice the initial Ag thickness in diameter) resulting from a balling of the film due to radiation-induced plastic flow in the same manor as seen during heavy ion irradiation of free-standing Ag films.

Concomitant with the plastic flow process, ballistic mixing disperses Ag into the SiO$_2$ matrix giving rise to nanoclusters. Irradiation also disperses Ag from larger particles redistributing it to the smaller ones. This leads to a monomodal size distribution.
distribution with a mean value less than 5 nm. Note that mixing of Ag atoms into the SiO$_2$ creates a concentration gradient with a maximum at the Ag film. Precipitation of Ag at some critical concentration should not result in Ag nanoclusters separated from the film but the growth of protuberances out from the initial Ag layer. However, such protuberances would be expected to disappear back into the film as a result of irradiation-induced flow. This would yield a zone denuded of Ag immediately below the Ag film with precipitation occurring below this zone. The depth resolution available from stereoscopic TEM was not sufficient to confirm the existence of such a zone.

Comparison of regions of the specimen that were continually irradiated with both the 400 keV Xe ion beam and the 300 keV electron beam with regions that were continually irradiated with the ion beam but only briefly irradiated with electrons (to record a photographic image), revealed large differences between the two regions. Both plastic flow and nanocluster formation are occur in the two cases, however both effects occur more rapidly with simultaneous ion and electron irradiation. The images and measurements reported here were all obtained without electron co-irradiation.

In conclusion, the *in-situ* TEM results reported in this paper demonstrate that irradiation of metal-insulator layers with energetic heavy ions results in the transformation of the metallic film into near spherical particles, about 30 nm in diameter, and the formation of metallic nanoclusters with diameters in the range 2 to 4 nm. Irradiation-induced plastic flow and irradiation-induced mixing are the processes driving the morphological changes.

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References

Figure captions

Figure 1  TEM micrographs showing changes in Ag film morphology as a result of irradiation with 400 keV Xe ions to different doses: a) unirradiated; b) 0.4; c) 3.0; d) $8 \times 10^{15}$ ions/cm$^2$

Figure 2  TEM micrograph showing morphology after $1.5 \times 10^{16}$ ions/cm$^2$. 
Figure 1

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Figure 2

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