Modification of a Gatan PIPS for Thin-Film Deposition

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Introduction

The resolution of the scanning electron microscope (SEM) is now such that we have the ability to examine the surfaces of bulk specimens at relatively high magnifications [1]. If it is desired to study a specimen that is an insulator by coating it with a conducting film, it is essential that the coating be thin with minimal structure, so that images are free from artifacts [2, 3]. A coating prepared by ion-beam sputtering satisfies these criteria. For transmission electron microscopy (TEM) work, thin amorphous support films mounted on a metal grid also may be prepared by ion sputtering.

In times where funding for capital equipment may be hard to find, one solution is to modify an existing ion sputtering machine for coating purposes. For applications where small specimens are to be examined, our Gatan Precision Ion Polishing System (PIPS, model 691) has proved useful in doubling as a sputter coater. This article describes a simple modification of the PIPS so as to permit the coating of bulk sample surfaces and the deposition of thin films of various materials. An advantage in using the PIPS for the latter purpose is the oil-free vacuum system, which allows films to be deposited with minimal fear of carbon contamination.

Materials and Methods

Our modification to the PIPS (Figure 1) involved replacing the airlock chamber cover with a unit made of brass, comprising a disc (C), 101 mm in diameter, on which was attached a simple device to permit rotation of the specimen to be coated. The sample (S) is mounted on a circular platform (B), 20 mm in diameter, using double-sided adhesive tape. The sample platform is at the end of a rod that rotates within a cylinder (J) that was attached at 45° to the cover, forming a vacuum-tight joint. An O-ring that could be compressed using a retaining nut (D) provided a vacuum seal to allow the sample-holder rod to rotate, aided by a Teflon ring (E). A drive ring (F) could be rotated, either by hand or using a belt connected to a geared-down electric motor, typically at ~6 rpm. Rotation is essential to ensure uniform coatings, particularly for samples with rough surfaces. Shadowing can be achieved, if required, by holding the sample stationary. Photographs of the modified unit are shown in Figure 2.

The sputter source was a disc about 3 mm in diameter (G), thin enough to be mounted on the regular specimen holder post. The source and substrates were typically ~15 mm apart. To speed the sputtering process, both guns were used to generate argon ion beams, tilted at angles of 10° toward the rotating target source material and operated at the maximum accelerating voltage of 6 kV. The source was sputter-cleaned for 5 minutes with the pneumatic shutter (H) closed, before coating commenced. The vacuum reading prior to deposition was normally ~10^{-3} Pa (~10^{-5} Torr) or better. Typical sputtering times for producing a uniform, thin coating were in the range 5 to 30 minutes, depending on the sputter source and thickness required.

Thin support films also could be made using various sources in the PIPS. Salt crystals (NaCl) are suitable substrates that allow the sputtered film to be floated off in water. Alternatively, plastic films of nitrocellulose or acetylcellulose (Bioden) may be used, in which case the substrate is dissolved using a suitable solvent such as acetone. The thin films were collected on Cu grids (200 or 400 mesh). Other metal grids should be used if it is necessary to avoid a Cu systems peak that might interfere with EDX analysis of a specimen containing Cu. Thin-film integrity was checked using TEM. We concluded that argon-ion sputtering in the PIPS produced very good films of uniform thickness that were either amorphous or nano-crystalline.

Results

Coating of insulators for SEM. In the absence of a high-resolution SEM, secondary electron (SE) images were obtained using our CM20FEG at 200 kV. Although such a high accelerating voltage is not typical for surface imaging, it had the advantage of providing an intense beam that could be focused to about 2 nm in diameter. Figure 3 shows images of insulating samples coated with a thin film of Pt,

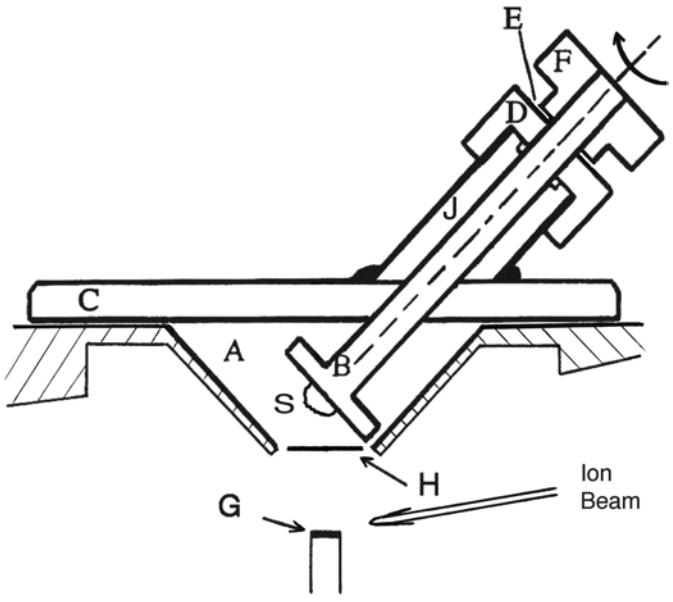

Figure 1: Cross section showing the replacement cover plate for the PIPS for depositing sputter coatings on small samples or making freestanding thin films: **A**: vacuum/sputtering chamber, **B**: platform support for specimens to be coated, **C**: vacuum chamber cover, **D**: locking nut to compress O-ring seal, **E**: Teflon washer, **F**: disc for specimen rotation, either manually or using an electrical belt drive, **G**: sputter source, **H:** PIPS shutter mechanism, **J**: support cylinder for drive shaft, **S**: specimen to be coated or substrate for thin-film deposition.

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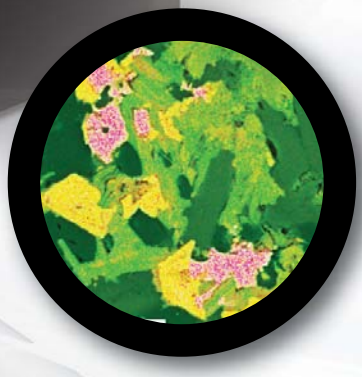

Geological thin section, elemental overlay
1 frame, 9.8 seconds

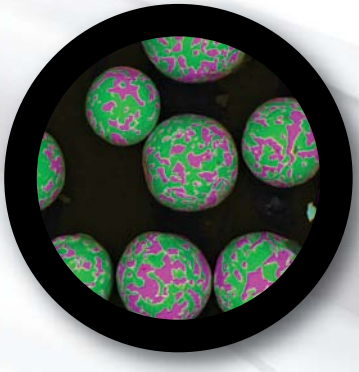

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Figure 2: Photographs of brass modification for the PIPS: (a) from above, (b) from below showing the specimen or substrate support disc, and (c) in position, replacing the PIPS cover plate (Catherine Bibby, CanmetMATERIALS).

produced using a Pt microscope aperture as the target. Figure 3a shows $Ni(OH)_2$ powder, which has important applications in electrodes for rechargeable batteries; its morphology was shown to be related to its performance. In other work, where the ability of an anodized Al alloy to bind with paint was examined, it was possible to observe very small features on the Pt-coated surface oxide (Figures 3b and 3c). Figure 3d shows spheres of SiO_2 fume, sputter-coated with elemental Pt.

Depositing thin films. A number of freestanding thin films were successfully prepared on both salt and plastic substrates using sputter targets of graphite, Cr, Pt, Al, Si, and SiO. The deposition rate was typically ~2 nm/minute. The results may be summarized as follows: (a) deposited films of Cr, Al, and SiO were fully amorphous, (b) Pt and Si films were nano-crystalline with grain sizes up to a few tens of nanometers, and (c) the carbon films were amorphous and less friable than the others.

Parallel-collection electron energy loss spectrometry (PEELS) analysis showed that there was a tendency for C and/or O to be incorporated into the non-carbon films during sputtering despite the oil-free vacuum system in the PIPS. This was most pronounced using plastic substrates and is attributed mainly to outgassing. This could be avoided if the PIPS chamber were pumped with the argon supply on for 1~2 hours before deposition in order to reduce the concentration of hydrocarbons in the vacuum chamber. This procedure also had the beneficial effect of purging the ion guns and proved particularly important for depositing reactive sputter coatings such as Cr and Al. To minimize the presence of hydrocarbons in the PIPS, the use of a salt substrate was therefore advantageous. Another technique that was useful for cleaning contaminants from the specimen chamber was to sputter a target of metallic Ti, which reacts readily with C and O, before depositing other elements.

Graphite targets produced amorphous carbon films that were effective for extraction replicas, which are useful for identifying precipitates without interference from the matrix in which they are formed [4, 5]. After suitable etching to cause the precipitate particles to stand proud above the matrix, they can be removed in two ways: (a) by directly depositing carbon onto the metal surface and etching to allow the carbon film to float off containing the embedded particles or (b) to first use a plastic film such as Bioden to strip off the particles, then deposit carbon onto the plastic surface and finally to dissolve the plastic to leave a carbon replica containing the particles. Because it is necessary to use small targets in the PIPS, we used the second method, leading to robust amorphous films in which extracted particles were readily discerned.

In order to analyze extracted precipitates containing carbon, it is helpful to use a film made of a low Z element other than carbon. Si films were tried, but they tended to break up when the plastic substrate was dissolved away. This was ascribed to residual stresses in the plastic after stripping, which could be eliminated by gently warming the film, for example, with an incandescent light bulb. However, the nano-crystalline nature of the films tended to lead to diffraction contrast that could detract from imaging the small extracted precipitates. SiO proved successful for carbon-free films, provided the presence of O did not interfere with the analysis.

A quite different application for a thin film of carbon came from experiments on thin TEM specimens made by embedding in resin and then sectioning in an ultra-microtome. These sections

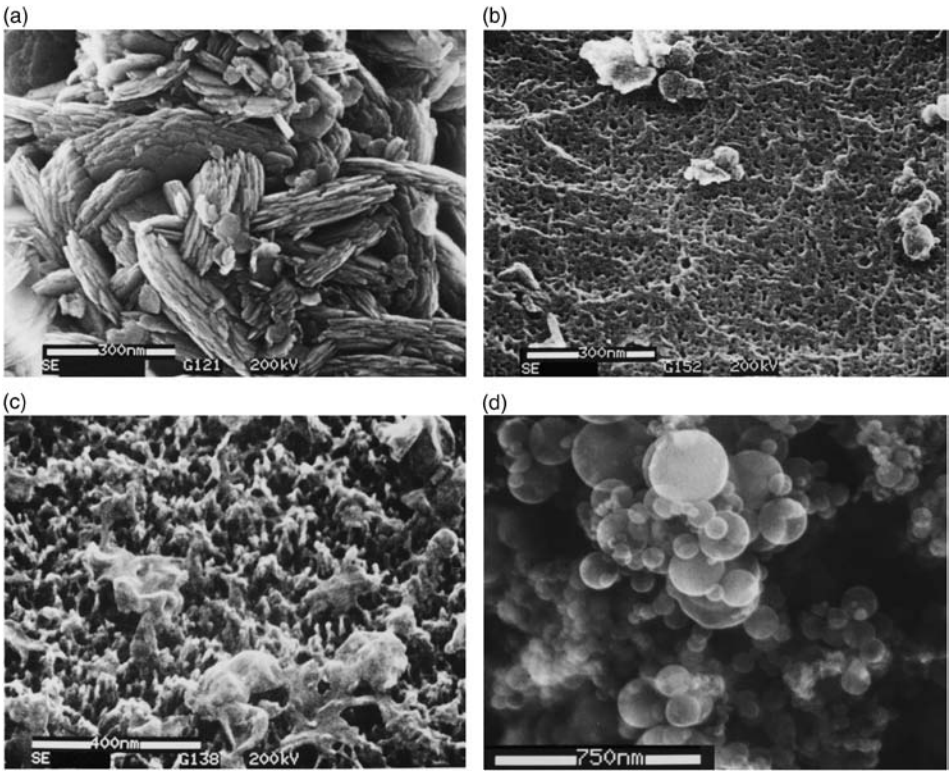

Figure 3: Typical SE images obtained from samples sputter-coated with Pt using the modified PIPS: (a) Ni hydroxide powder, manufactured for use in the electrodes of rechargeable Ni metal hydride batteries, (b) an anodized Al alloy, showing small pores designed to assist in the adherence of surface coatings, (c) an anodized Al alloy showing surface protuberances on the nanometer scale, and (d) spheres of SiO_2 fume.

were sometimes very unstable in the electron beam. This was overcome by the deposition of a very thin film of carbon on one surface of the sections, readily accomplished in the PIPS using deposition times of the order of minutes. The resulting C surface coatings were without visible structure, permitting high-resolution imaging and EELS and EDX mapping with no compromise to the normal operating conditions of the microscope.

Conclusions

In the absence of a dedicated sputter coater, an ion-beam machine such as the Gatan PIPS, designed for making TEM thin specimens, can be modified to produce thin films from virtually any solid target source. Applications include (a) depositing conducting coatings to permit examination of insulators in the SEM and (b) making freestanding films supported on a TEM grid, for example, for producing extraction replicas. Of the films studied in our lab, Pt and Si were nanocrystalline, whereas C, SiO, Cr, and Al were fully amorphous. Special precautions were needed in depositing reactive metals such as Cr and Al in order to minimize contamination. Despite the oil-free vacuum system in the PIPS, the presence of low levels of C, N, and O could not be avoided completely. Significant contamination from hydrocarbon outgassing was observed when reactive films were made using plastic substrates such as Bioden, but this could be overcome by first purging the vacuum chamber.

Acknowledgments

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