TEM specimen preparation of semiconductor–PMMA–metal interfaces

P. Thangadurai, Yulia Lumelsky, Michael S. Silverstein, Wayne D. Kaplan*

Department of Materials Engineering, Technion, Israel Institute of Technology, Haifa, 32000, Israel

ARTICLE DATA

Article history:
Received 1 November 2007
Received in revised form
24 February 2008
Accepted 29 February 2008

Keywords:
TEM
EELS
FIB
PMMA
Interfaces

ABSTRACT

Transmission electron microscopy (TEM) cross-section specimens of PMMA in contact with gold and Si were prepared by focused ion beam (FIB) and compared with plan-view PMMA specimens prepared by a dip-coating technique. The specimens were characterized by TEM and electron energy loss spectroscopy (EELS). In the cross-section specimens, the thin films of PMMA were located in a Si–PMMA–Au multilayer. Different thicknesses of PMMA films were spin-coated on the Si substrates. The thickness of the TEM specimens prepared by FIB was estimated using EELS to be 0.65 of the plasmon mean-free-path. Along the PMMA–Au interface, Au particle diffusion into the PMMA was observed, and the size of the Au particles was in the range of 2–4 nm. Dip-coating of PMMA directly on Cu TEM grids resulted in thin specimens with a granular morphology, with a thickness of 0.58 of the plasmon mean-free-path. The dip-coated specimens were free from ion milling induced artifacts, and thus serve as control specimens for comparison with the cross-sectioned specimens prepared by FIB.

© 2008 Elsevier Inc. All rights reserved.

1. Introduction

Electron microscopy of soft materials such as polymers is difficult for a number of reasons. In electron or ion microscopes it is difficult to form images of polymer-based samples because they are usually insulators, and hence suffer from charging effects under the electron/ion beam. Soft materials are also very sensitive to electron and ion beam induced irradiation damage. Low vacuum scanning electron microscopy (LVSEM), augmented with a field emission gun (FEG) electron source, provides high brightness even at low accelerating voltages of the order of 1–2 kV, so that it is possible to investigate non-conducting materials without a conductive coating [1]. The irradiation damage to polymers depends on the mean atomic number, the density of the polymer and substrate, the sample thickness, and the accelerating voltage of the electron/ion beam [2]. Low accelerating voltages result in irradiation damage due to the larger average scattering cross-sections. High accelerating voltages (e.g. ~50 kV for 1 μm thick polymer films on a substrate) the volume from which backscattered electrons is generated will be larger, leading to irradiation damage in a large volume of the sample [2]. Therefore, optimal accelerating voltages, which reduce charging and limit irradiation damage, must be developed for each material system. Similar issues must be addressed for nanometer length-scale feature-sizes formed in polymer resists during e-beam patterning where proximity effects, including the diffusion length of backscattered electrons, limits dimensional control [3].

In transmission electron microscopy (TEM), one of the main difficulties in studying polymers (or soft materials) is specimen preparation. Specimen preparation for TEM involves challenging procedures, which often need to be developed and optimized for specific material systems. In general, there are two types of sampling orientations required for TEM studies: plan-view and cross-section. Plan-view specimens are usually relatively simple to prepare as long as the source material is bulk. Cross-sectional specimens are often prepared for microstructural investigations of interfaces between dissimilar materials, and can be difficult to prepare, depending on the material system of interest. In general, while the preparation of
TEM specimens from inorganic materials is well established, soft (organic) materials such as polymers require tedious procedures and careful analysis of artifacts introduced by the specimen preparation procedure. TEM is a valuable technique in polymer science, but the preparation of thin (50–100 nm) electron-transparent specimens requires the development of methods for which artifact formation is understood.

Existing TEM specimen methods include ion milling [4–6], electropolishing [7], ultramicrotomy [8], tripod polishing [9,10], cleaving [11] and focused ion beam (FIB) milling [12,13]. Conventional methods of mechanical thinning followed by ion milling are generally acceptable for ceramics, metals, and semiconducting material systems [11], but their use is questionable for preparing TEM specimens from soft materials such as polymers and photoresists. The main difficulty with soft materials is irreversible deformation introduced by mechanical thinning.

Philipp et al. used conventional thinning and cleaving after sandwiching to prepare cross-sectional specimen of Au/Langmuir–Blodgett (LB) film/Au multilayers on SiO2 substrates [11], in which Au was used as the electrode for electrical characterization of the LB film. The standard method of thinning using ion milling for cross-sections induces atomic diffusion, especially at interfaces, which is an unwanted effect in the specimen preparation process. Use of FIB to prepare cross-sectional (and site-specific) TEM specimens was developed in the 1980s, and now plays a major role in studying many complex material systems [14–19]. When FIB is combined with the “lift-out” TEM specimen preparation method, potential artifacts introduced by mechanical pre-thinning can be avoided [20]. While FIB provides site-specific, thin TEM specimens, it does introduce artifacts, mostly in the form of amorphous regions in crystalline specimens [21].

In this work, two types of TEM specimen preparation techniques are compared for PMMA as a representative for polymer-based materials. The first was developed to prepare cross-section specimens of a semiconductor–polymer–metal multilayer system (Si–PMMA–Au), and the results are compared with plan-view PMMA specimens. This multilayer system is also important for the study of interfaces between semiconductors and polymers, and between polymers and metals. These interfaces have numerous device applications, including the characteristic structure of polymer photovoltaic cells and polymer light-emitting diodes (LED) [22]. In addition, the chemical composition, thickness, and roughness of the Si–polymer–metal layers and their interfacial integrity are important parameters for the performance of devices. The interface roughness influences light transmission, the work function of electrodes, and homogeneity of the current density. The test polymer used in both cases of this study is polymethylmethacrylate (PMMA) which is an amorphous polymer. The motivation to study PMMA using electron microscopy is because it is a typical representative of soft organic materials, and technologically important for optical and electron beam lithographies [23–25]. In this study, cross-sectional Si–PMMA–Au and plan-view PMMA specimens were prepared by FIB and dip-coating, respectively. In order to investigate their suitability for electron microscopy, their microstructures were studied.

2. Experimental Methods

To prepare TEM specimens of PMMA using FIB, PMMA (Palram Industries Ltd., Israel) was deposited on Si wafers, followed by a thin coating of gold. PMMA solutions of different concentrations (0.8, 4 and 5 wt.% of PMMA) in chlorobenzene (C6H5Cl) were prepared and spin-coated on Si wafers (SCS, G3-8 Spin Coat, Specialty Coating System Inc., USA) at a spinning speed of 3000 rpm with 30 s dwell time, followed by solvent evaporation for 1 min at 150 °C in air (which is part of the standard PMMA process). The different solution concentrations were used to reach different thicknesses of the PMMA layers. The PMMA was then coated with Au using a Polaron sputter coater (Ar+ ion sputtering). A dual-beam FIB (Strata 400 s, FEI) equipped with a field emission gun (FEG) electron source (operated at 30 kV), a Ga+ ion beam (2–30 kV), an in-situ nanomanipulator (Omniprobe) and scanning transmission electron microscopy (STEM) detectors (bright field, dark field and high angle annular dark field (HAADF) modes) was used to prepare cross-sectional TEM specimens from the multilayer samples. The energy and current of both beams were optimized to reduce obvious specimen damage during TEM specimen preparation. The accelerating voltage and current of the incident e-beam was maintained at

![Fig. 1 - Secondary electron SEM micrographs of a Si–PMMA–Au multilayer after forming a U-cut in the FIB.](https://example.com/fig1.png)
5 kV and 1.6 nA, respectively, throughout the entire process. An incident ion beam accelerating voltage of 30 kV, with an ion current ranging from 2.8 nA to 23 pA, was used during initial milling. Final polishing in the FIB was conducted at 5 kV and 16 pA, followed by 2 kV and 10 pA.

Before preparing thin lamellas, the surface of the multilayer sample was coated with Pt in the FIB, first by e-beam deposition (5 kV, 1.6 nA) and then by ion beam deposition (30 kV, 0.46 nA). In general, the Pt coating prevents ion damage of the surface and reduces charging. 500–700 nm thick lamellas were formed by milling trenches on both sides of the region of interest (30 kV ion accelerating voltage, 2.8 nA ion beam current), followed by a U-cut to partially remove the lamella from the substrate (Fig. 1) [26,27]. The lamella was lifted-out from the substrate, and attached to a Mo TEM grid mounted on a flip-stage in the FIB, using the nanomanipulator. The lamella was further thinned by FIB to a thickness of ~50 nm for conventional TEM. The specimens were then ion-polished in the FIB, first at 5 kV and 16 pA, followed by polishing at 2 kV and 10 pA, to remove ion beam induced damage from the previous stages of specimen preparation. The final thickness of the specimen was estimated in the FIB using secondary electrons induced by the incident electron beam. The relative thickness was monitored during thinning by recording STEM micrographs at an incident electron accelerating voltage of 30 kV.

Plan-view specimens of PMMA were prepared by dip-coating. A solution of 0.5 wt.% PMMA in acetone was prepared, and 300 square mesh Cu TEM grids were dipped into the solution and dried in air. Due to the surface energy of PMMA, the films form a concave shape between the Cu grid lines, resulting in a thin region at the center.

The TEM specimens were characterized using a Tecnai G² T-20 (FEI) TEM operated at 200 kV, and equipped with STEM and EDS detectors. Analytical studies by electron energy loss spectroscopy (EELS, Gatan Image Filter) were conducted in a Tecnai G² F-20 TEM. High resolution TEM studies were conducted in a monochromated and aberration corrected FEG-TEM (Titan 80-300 S/TEM, FEI) with a variable accelerating voltage (from 80 to 300 kV).

3. Results and Discussion

3.1. FIB Specimen

Fig. 2 presents typical STEM bright field (BF), dark field (DF) and high angle annular dark field (HAADF) micrographs of the FIB specimen (Si–PMMA–Au), acquired at an electron accelerating voltage of 30 kV in the FIB. The PMMA layer appears white and dark in the bright field and dark field images, respectively. The gold layer appears darker since it is heavier than PMMA.

Fig. 3 – BF TEM micrographs of FIB cross-section specimens prepared from Si–PMMA–Au. (a) 0.8 wt.% spin-coated PMMA and (b) 5 wt.% spin-coated PMMA. The dashed circles indicate the Au particles. The Pt coating, deposited in the FIB to minimize ion damage of surface of the sample, is indicated.
and less transparent to electrons relative to PMMA and Si. In HAADF incoherently scattered electrons are used to form the image, and hence the brightness of the image is proportional to the mean atomic number of the region. Thus Au has a brighter contrast compared to the other layers in Fig. 2c. These micrographs show good electron transparency which is indirect evidence of a specimen thickness suitable for TEM.

Fig. 3 presents typical TEM micrographs of the cross-section FIB specimens in which the PMMA layer was spin-coated with 0.8 wt.% (Fig. 3a) and 5.0 wt.% (Fig. 3b) PMMA. The fact that the specimens are electron-transparent is evident from the Au layer, because the Au grains are clearly visible. The PMMA layer shows good contrast and the interface between Si and PMMA is well resolved and flat, which results from the spin-coating process and the 150 °C post-deposition bake. While the interface between PMMA and Au is slightly rough, no interfacial voids were detected. Additional details from the interfaces are visible in the high resolution TEM micrographs presented in Fig. 4 (5 wt.% PMMA). As discussed above, the PMMA/Si interface is smoother than the Au/PMMA interface. The thickness of this specimen was measured using EELS from the center of the PMMA film. A typical EEL spectrum of the FIB specimen containing low-loss and C–K core-loss edges is shown in Fig. 5. The thickness of the FIB specimens was determined from the ratio of the integrated intensities of the total low-loss spectrum to the zero loss peak (ZLP) [28], resulting in 0.65Å, where $\lambda$ is the plasmon mean-free-path of PMMA. A background correction to the core-loss edge was made using a power-law function of the form $I = A \cdot E^{-r}$, where $A$ and $r$ are fitting parameters [28].

In addition to obtaining thin TEM specimens by FIB, it is also worthy to note that the more or less uniform PMMA film thickness, obtained from spin-coating and an integral part of the specimen preparation method, was not damaged during the FIB milling process. Conventional thinning can result in a non-uniform film thickness, for example in the case of Au/Langmuir–Blodgett film/Au multilayers on SiO$_2$ [11] where non-uniformity was introduced by the TEM specimen preparation method. In the present case, the PMMA film thickness measured from Fig. 3(a) and (b) is in the range of 13–16 nm and 51–54 nm, respectively.

The metal–polymer interfaces and their stability against inter-diffusion are important in the use of polymers for the protection and interconnection of a variety of electronic components, at both the chip and packaging levels. In general, reactive metals form relatively sharp interfaces with polymers, whereas metals such as Ag and Au show pronounced diffusion, especially at low evaporation rates and at temperatures in the range of 350 °C [29,30]. In this case, we observed crystalline particles, 2–4 nm in diameter, diffused into the PMMA along the top surface of the PMMA layer, as seen in Fig. 3b (marked by circles). This form of diffusion has already been reported [11,31,32]. These particles were characterized using phase contrast in the TEM (see Fig. 4), and identified as Au from their (111) lattice spacings (0.23±0.01 nm) (JCPDS Card 04-0784).

Fig. 4—HRTEM micrographs of (a) Au–PMMA and (b) PMMA–Si interfaces (5 wt.% spin-coated PMMA). Two Au particles located in the PMMA film are marked in (a).

Fig. 5—EELS spectrum of the FIB specimen, Si–PMMA–Au (0.8 wt.% spin-coated PMMA). The intensity range is different for the ZLP and core-loss peaks.
3.2. Dip-Coated Specimens

Low magnification TEM micrographs of dip-coated specimens of PMMA are presented in Fig. 6. Fig. 6 shows the granular morphology of PMMA formed by dip-coating. The PMMA is attached to the bars of the Cu TEM grid and extend to the center of the mesh. The film at the center of the mesh is thin enough to be investigated by TEM. The dark contrast in Fig. 6a and b is from overlapping PMMA films.

Fresnel fringes are visible in Fig. 6b, around the edges of some of the PMMA. The appearance of Fresnel fringes only at some of the PMMA–vacuum interfaces indicates height differences for different regions in the sample, leading to a relative change in objective lens defocus. The inset in Fig. 6b is a selected area diffraction (SAD) pattern acquired from the central region of the same figure. The diffuse ring pattern of the SAD characterizes the amorphous nature of PMMA. One region of the PMMA, arrowed in Fig. 6b, contains a white bubble-like morphology, which is likely damage induced by electron beam irradiation. These defects are induced by partial degassing of PMMA, and their appearance and size are a function of electron dose.

A typical low-loss EEL spectrum of the dip-coated specimen, including the ZLP, is shown in Fig. 7, from which the specimen thickness was estimated to be 0.58 Å. The plasmon peak does not exhibit any higher order peaks, which indicates the absence of plural scattering. This confirms single scattering of electrons in these specimens, indicating their suitability for TEM studies. While the PMMA thickness varies slightly from location to location in the TEM specimen, numerous regions thin enough for TEM studies were found.

The core-loss edges shown in Fig. 7 are the characteristic K-ionization edges of carbon and oxygen, which are components of PMMA \([\text{C}_8\text{O}_2\text{H}_8]_n\). Estimation of the specimen thickness and the background correction to the core-loss edges were performed in a similar way as discussed earlier for the FIB cross-section specimen. The plasmon peak observed at 21 eV is correlated to the collective excitations of free electrons.

A typical high magnification TEM micrograph of a dip-coated specimen of PMMA is presented in Fig. 8. This image was acquired from one of the thinnest regions and shows the morphology of the amorphous polymer. It is important to note that no physical damage was observed in the PMMA during the course of TEM investigations, except for small bubble-like structures, as discussed earlier.

Ultramicrotomy is a well known method for TEM specimen preparation of soft materials, but damage due to plastic deformation is a limiting factor of this method. Patrick et al. used two methods; i) chlorosulfonation and sectioning and ii) permanganetic etching and replication for the preparation of polymer TEM specimens with a success rate of 40%. In our attempts to prepare cross-sectional polymer TEM specimens of the Si–PMMA–Au multilayers by conventional...
mechanical thinning and ion milling, the polymer layer was extensively damaged. The present method has an important advantage in that the specimens are almost completely free from artifacts induced by the preparation method. In addition, this procedure resulted in almost 100% success for the preparation of thin TEM specimens.

4. Summary and Conclusions

Two TEM specimen preparation methods are suggested for PMMA. While FIB has been successfully used for preparing TEM specimens of hard materials, this work showed its application to prepare cross-sectional TEM specimens of soft materials. When the thickness of the lamella was less than 50 nm, an ion beam current of more than 46 pA was found to result in irradiation damage. Dip-coating of PMMA on Cu TEM grids was proven to be a viable approach for the preparation of control specimens, where ion milling is not required. Both these methods avoid mechanical deformation, which is very common in conventional TEM specimen preparation. The thickness of the TEM specimens prepared by both techniques was found to be less than the plasmon mean-free-path. The advantage of the dip-coating approach is that it produces TEM specimens without ion milling, which can be compared with the cross-section specimens prepared by FIB to identify ion beam induced defects.

Acknowledgements

The authors thank M. Katz for technical assistance. This work was conducted with the partial support of the European 6th Framework specific targeted research project RIMANA (Radical Innovation MAskless NAnolithography), contract No. 17133 (www.rimana.org).

REFERENCES


