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Development of Multilayers for Soft X-ray Mirrors and Depth Analysis

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Two types of multilayers have been developed in which the thickness is controlled at the sub-angstrom level. One type is for soft X-ray mirrors. For a Mo/Si multilayer, the measured peak reflectivity is about 69% at a wavelength of around 13 nm and an incident angle of 88°; and for a Cr/C multilayer, it is about 19% at a wavelength of 6.4 nm and an incident angle of 88°. The other type is for use as a reference material for shallow depth profiling in SIMS. Periodically BN-delta-doped Si with a short period ranging from 1.4 to 5.0 nm exhibits periodic B ion peaks under SIMS analysis.
Key words: multilayer, soft X-ray mirror, SIMS, depth profiling, reference material

1. INTRODUCTION

Multilayers consisting of very thin alternating layers of different materials with thicknesses controlled at the sub-angstrom level are useful for a variety of applications. One is reflective optical devices, such as mirrors for extreme ultraviolet (EUV) light and X-rays [1]. These are useful in fields as varied as EUV lithography (EUVL) [2,3], X-ray photoelectron spectroscopy (XPS) [4-6], X-ray lasers [7], X-ray microscopy [8,9] and X-ray astronomy[10]. For these applications, reflectivity is the most critical parameter determining the performance of a multilayer mirror. A high reflectivity requires smooth interfaces and a precise periodic structure.

Another application is reference materials for depth analysis. Depth profiling is widely used in the surface analysis of materials such as semiconductors and magnetic devices. The quality of the analysis depends on the adjustment of the apparatus, such as the ion gun, which accelerates ions so that they can etch the surface of the material. To optimize the apparatus for depth profiling, multilayered materials with a precisely controlled periodic structure are required.

The use of magnetron sputtering to fabricate multilayers provides the following advantages: (a) a high deposition rate and long-term stability, (b) good control of the thickness, (c) applicability to insulators as well as metals, (d) deposition over a large area with good uniformity, and (e) good reproducibility.

In this study, two types of multilayers were fabricated by magnetron sputtering: one for soft X-ray mirrors, and the other for a reference material for shallow depth profiling in SIMS.

2. FABRICATION

Our sputtering system consists of two sputtering sources, a rotating substrate table that spins the substrate, a system for controlling the speed of rotation, and shutters. The substrates are mounted on the table and alternately exposed to individual, well-isolated sources [11].

Multilayers were deposited on 4-inch-diameter Si wafers in an argon atmosphere without sample heating. The deposited materials are amorphous. The thickness uniformity of fabricated multilayers was examined with a surface profiler after the formation of grooves on the multilayer by a lift-off process. In the region within a 60-mm diameter from the center of a wafer, the multilayer thickness was found to be very uniform, with a variation of ± 1% or less [12].

3. SOFT X-RAY MULTILAYER MIRRORS

3.1 Multilayers for a wavelength of around 13 nm

Mo/Si multilayers for a wavelength of around 13 nm are useful in such fields as X-ray lasers, microscopy, astronomy, and EUVL. For these applications, the reflectivity of the multilayer mirror is critical. Figure 1 shows the soft X-ray reflectivities of Mo/Si multilayers fabricated with our magnetron sputtering system. They

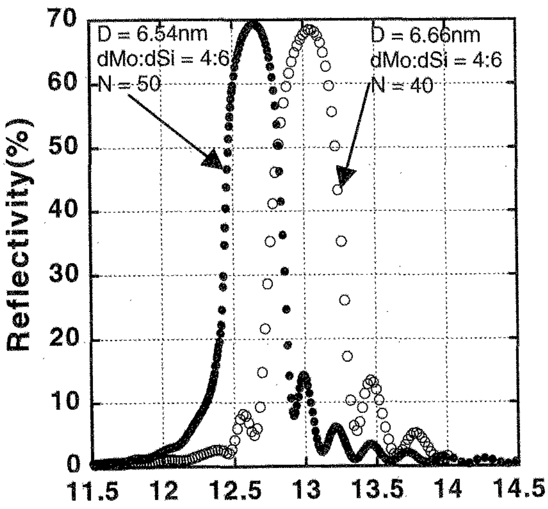

Figure 1. Measured reflectivities of Mo/Si multilayers at an incident angle of 88°. Closed circles: 69.3% @ $\lambda = 12.6$ nm. Open circles: 68.4% @ $\lambda = 13$ nm.

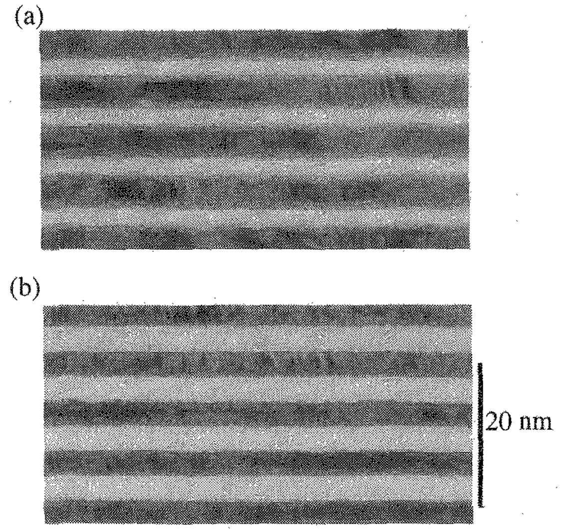

Figure 2. Cross-sectional TEM image of (a) Mo/Si multiplayer and (b) Mo/C/Si/C multilayer.

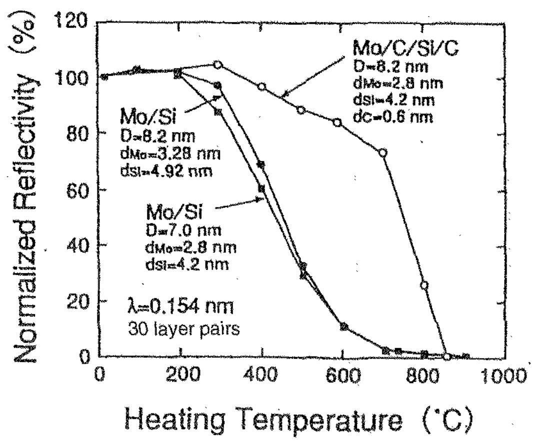

Figure 3. Relationship between normalized Cu-Kα first-order Bragg-peak reflectivity of Mo/Si and Mo/C/Si/C multilayers and heating resistance.

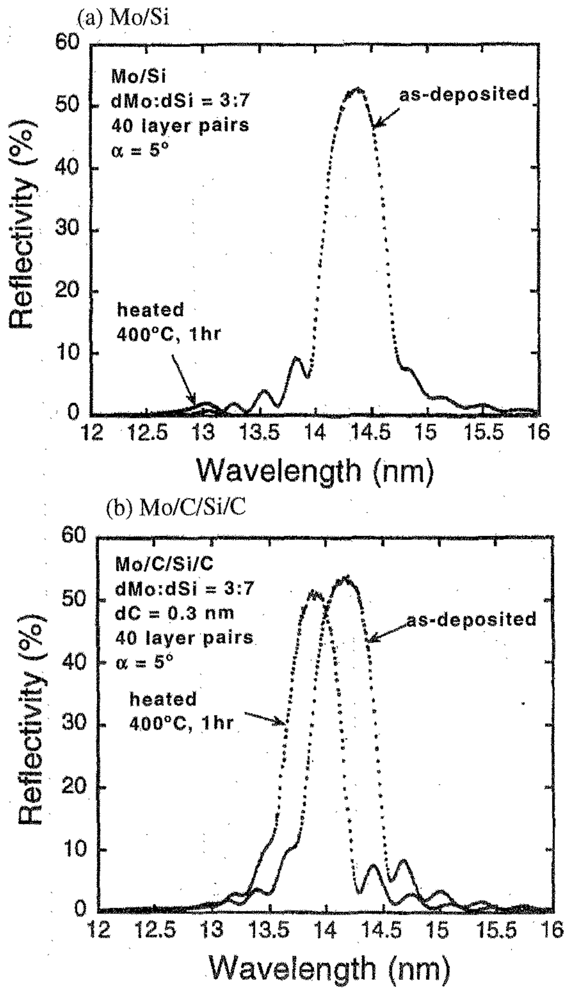

Figure 4. Measured reflectivities of as-deposited and 400°C-annealed (a) Mo/Si multilayers and (b) Mo/C/Si/C multilayers at an incident angle of 85°. Each has 40 pairs of layers. The period is 7.2nm forthe Mo/Si multilayer and 7.3nm for the Mo/C/Si/C multilayers.

were measured on Beamline 6.3.2 of the Advanced Light Source at LBNL [13], and the current from a Si photodiode was used to determine the intensity of the reflected and incident beam. The absolute reflectivity was obtained by dividing the intensity of the reflected beam by that of the incident beam. The reflectivities were found to be about 68-69% at a wavelength of 13 nm and an incident angle of 88°.

One way to improve the thermal stability and boost the reflectance of Mo/Si multilayers is to block the interdiffusion of the Mo and Si by interposing a layer of C [13], B_4C [14], SiO_2 [15] or some other material between the Mo and Si layers. Figure 2 shows cross-sectional TEM images of Mo/Si and Mo/C/Si/C multilayers. Clearly, the latter has smoother interfaces. Figure 3 shows the relationship between the normalized Cu-Kα first-order Bragg-peak reflectivity of Mo/Si and Mo/C/Si/C multilayers and heating resistance. The reflectivity of the Mo/Si multilayers dropped markedly after annealing above 300°C in Ar atmosphere and 1 hour; and after annealing at 600°C, it fell to only 11-12% of the value for an as-deposited sample. On the other hand, for the Mo/C/Si/C multilayer the change was much smaller. The reflectivity remained about 80% of the value for an as-deposited sample, even after heating at 600°C. Figure 4 shows the soft X-ray reflectivities of as-deposited and annealed Mo/Si and Mo/C/Si/C multilayers. The annealing was performed at 400°C in Ar atmosphere and 1 hour. Since the direct beam was not sufficiently monochromatic in these measurements, the values obtained are smaller than the actual values. The peak reflectivity of an as-deposited Mo/Si multilayer was 52.8% at a wavelength of 14.4 nm. After annealing, it dropped to 2.0%, and there was a large decrease in the peak wavelength to 13.0 nm. On the other hand, the peak reflectivity of an as-deposited Mo/C/SiC multilayer was 54.0% at a wavelength of 14.2 nm. Annealing only reduced this to 51.3%, and there was a slight decrease in the peak wavelength to 13.9 nm.

3.2 Multilayers for a wavelength of around 6 nm

6-nm X-rays are useful for taking XPS spectra of elements like silicon and boron. However, the

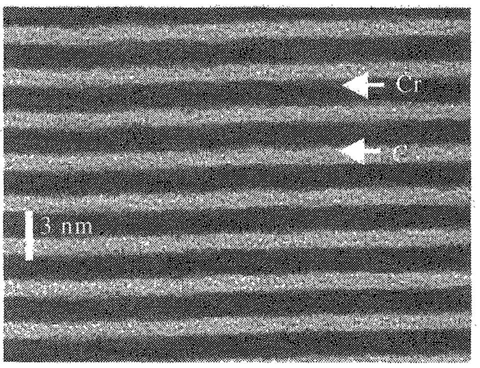

Figure 5. Cross-sectional TEM image of Cr/C multilayer

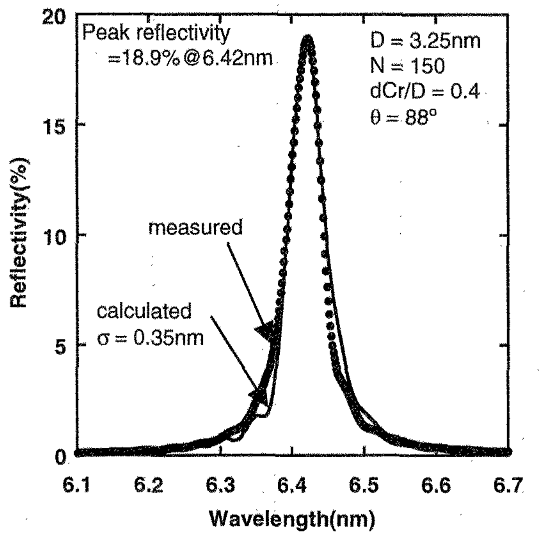

Figure 6. Measured and calculated (fitted) reflectivity of Cr/C multilayer.

reflectivity of multilayer mirrors is generally very low in the 6-nm region for two reasons. First, the optical constant for this wavelength is not suitable for high reflectivity, because this wavelength is between the carbon absorption edge (4.47 nm) and the boron absorption edge (6.76 nm). Second, the layers of multilayer mirrors for a wavelength of 6 nm are very thin (around 1.5 nm), which causes the materials to easily aggregate, thus making it difficult to obtain the smooth interfaces required for a high reflectivity. We previously designed Co_xCr_{1-x}/C multilayer mirrors with a comparatively high reflectivity at around normal incidence, and evaluated the structure of the multilayers by means of TEM and the soft X-ray reflectivity [13]. Figure 5 shows a cross-sectional TEM image of a Cr/C multilayer. Clearly, the interfaces are very smooth. The reflectivity is 18.9% at a wavelength of 6.4 nm and an incident angle of 88° (Fig. 6). Moreover, finding the best fit for the reflectance profile yielded an interface roughness of 0.35 nm, assuming the bulk values for the densities of the Cr and C layers. The interface roughness is smaller than that of other Co_xCr_{1-x}/C multilayers.

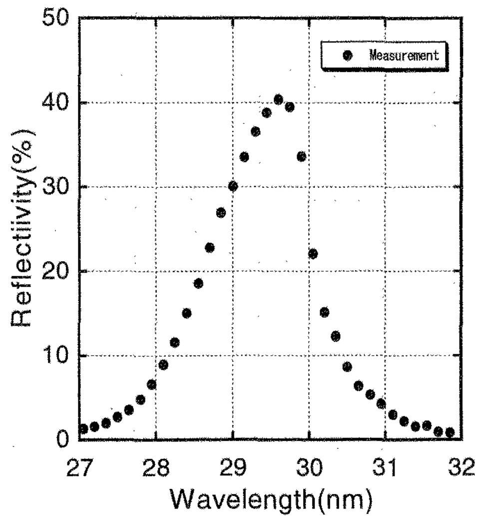

Figure 7. Measured reflectivitiy of Mg/SiC multilayer for an incident angle of 88°.

3.3 Multilayers for a wavelength of around 30 nm

Mg/SiC multilayers for a wavelength of around 30 nm have application to ultraviolet photoelectron microscopy, lasers, astronomy, and so on. However, it is difficult to deposit a smooth thin film of Mg due to its low melting point and high vapor pressure. So, the structure and reflectivity of a fabricated sample were evaluated at a wavelength of around 30 nm. Figure 7 shows the measured peak reflectivity to be 40.6% at a wavelength of 29.7 nm and an incident angle of 88°. To evaluate the heat resistance, samples were heated in an infrared furnace for one hour at temperatures from 250°C to 400°C in an Ar atmosphere. The reflectivity remained constant up to a temperature of 300°C, but decreased above that temperature.

4. BN-DELTA-DOPED REFERENCE MATERIAL FOR SHALLOW DEPTH PROFILING IN SIMS [12]

Multiple delta-doped layers in silicon are used to evaluate the performance of shallow depth profiling with SIMS and for depth calibrations [17]. For this purpose, we developed multiple short-period BN delta-doped layers in silicon for use as a reference material in shallow depth profiling by SIMS. To optimize the material, we fabricated two series of BN/Si multilayers and examined them.

First, to determine the optimal thickness of the BN layers, a series of BN/Si multilayers was fabricated in which the thickness of the Si layer was almost constant and the thickness of the BN layer had values ranging from 0.1 to 0.002 nm. The evaluation tools were TEM and SIMS. This series was designed to investigate how the thickness of the BN layer affected the ion yield in SIMS profiles. Figure 8 shows a cross-sectional TEM image of a sample in which the BN layers were 0.1 nm thick and the Si layers were 18 nm thick. These results demonstrate that 0.1-nm-thick BN layers are a suitable reference material for characterization by TEM. However, this sample exhibited significant enhancement of the Si ion intensity in the SIMS profile. This enhancement can be avoided by making the BN layers thinner than around 0.02 nm, although at that thickness

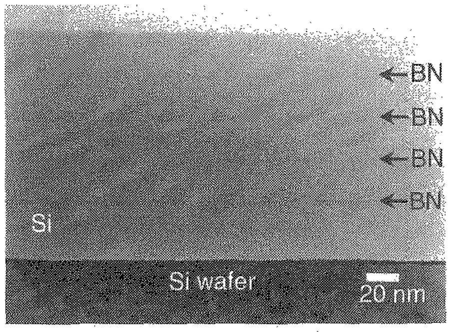

Figure 8. Cross-sectional TEM image of multiple BN delta layers. Thickness of BN layer: 0.1 nm. Thickness of Si layer: 18nm.

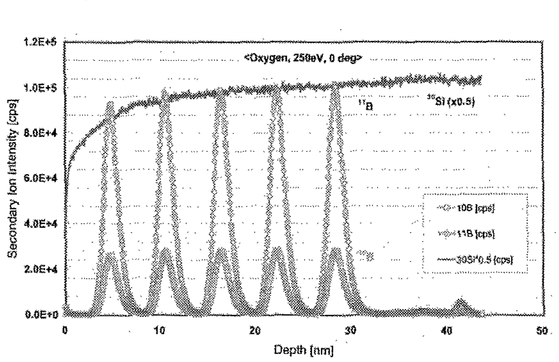

Figure 9. High resolution SIMS depth profile of multiple short-period BN delta layers. Thickness of BN layer: 0.05 nm. Thickness of Si layer: 5nm. The data was obtained using 250 eV O_2^+ at 30° incidence.

they can no longer be observed by TEM. As a compromise, we selected a thickness of 0.05 nm for the BN layers of the reference material. These layers are still discernible, but the contrast is very low.

Second, in order to determine the sputtering rate and depth resolution near the surface in SIMS depth profiling, a structure with a short period is necessary as a marker for the depth scale. So, a second series of samples was fabricated in which the thickness of the Si layer varied from 1.4 to 18 nm and the thickness of the BN layers was a constant 0.05 nm. They were analyzed by high-resolution SIMS. Figure 9 shows the results for multiple short-period BN delta-doped layers and Si layers 5 nm thick. The modulation of the boron ion intensity is very clear. The peak height and width are uniform for all the layers. The delta layer spacing is also uniform, except for the spacing between the surface and first peak. The position of the first peak reflects the fact that the sputtering rate is not uniform in the initial stages of ion bombardment, the assessment of which is one of the major purposes of this type of reference material. The depth profile of the 1.4-nm sample show a small but periodic modulation of the B ion intensity. Since the modulation amplitude is constant for all the layers, this material should be very useful. A detailed analysis of the sputtering rate has been reported elsewhere [18].

5. SUMMARY

Two types of multilayers consisting of very thin alternating layers of different materials have been developed: one type is for soft-X-ray multilayer mirrors, and the other is a reference material for depth profiling. Both types are fabricated by sputtering. Fabricated soft-X-ray multilayer mirrors employing Mo/Si, Cr/C, or Mg/SiC multilayers exhibit a high reflectivity and smooth interfaces, and are useful for XPS and X-ray laser applications, etc. A periodically BN-delta-doped Si reference material with a short period of 1.4-5.0 nm exhibits a periodic B ion peak. These results indicate that this type of multilayer should be very useful for shallow depth profiling in SIMS.

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