Depth profiling of polycrystalline multilayers using a Buckminsterfullerene projectile

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Depth resolution of 5 nm was achieved on a Ni:Cr multilayer structure using 15 keV C_{60}^{+} ion bombardment for depth profiling. The results, acquired by monitoring the sputtered neutral flux of Ni and Cr atoms, are of equivalent quality to those achieved using low-energy obliquely incident atomic beams with sample rotation. The reason behind these improved results is shown to be due to the unique ability of this cluster ion to remove material without regard to crystallographic orientation, hence reducing the buildup of topography. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1764594]

Sputter depth profiling is a well-established method for determining the chemical composition of a solid as a function of depth beneath the surface.[1] The depth resolution achievable with this method largely depends upon the parameters of the ion beam used to erode the sample as well as upon the nature of the analyzed material itself. In particular, it has been demonstrated that polycrystalline materials pose a severe problem, since their erosion rate generally depends upon the crystallographic orientation of the bombarded surface and is therefore different for different grains.[2–7] This effect leads to the buildup of topography which severely limits depth resolution. A prominent example for this class of materials is a Ni:Cr multilayer on Si.[8–10] For these samples, it has been demonstrated that depth resolution of a few nanometers can only be achieved and maintained throughout the removal of the complete layer stack if low-energy primary ions are employed in connection with oblique ion incidence, sample rotation and, in some cases, oxygen flooding during the erosion. In this work, we show that similar resolution is directly achievable if the analysis is performed with a high-energy Buckminsterfullerene (C_{60}) cluster ion projectile. These projectiles, as a consequence of their special icosahedral geometry and 0.7 nm diameter, deposit most of their kinetic energy near the surface without insult to deeper layer structure. With high kinetic energy beams, erosion rates and lateral resolution are greatly improved, opening possibilities for sputter depth-profiling technology.

Experiments were performed using a time-of-flight secondary ion mass spectrometer (TOF-SIMS) equipped with a C_{60}^{+} ion source[11] and a liquid metal Ga^{+} ion source.[12] To assess the usefulness of cluster projectiles, results obtained with the C_{60}^{+} ion beam and with the atomic Ga^{+} ion beam are directly compared using an impact kinetic energy of 15 keV in both cases. To avoid the well-known secondary ion mass spectrometry matrix effect and enhance the intensity of the measured signal, neutral species sputtered from the sample surface are ionized by femtosecond laser pulses[13] and detected by the TOF-SIMS. The Ni:Cr multilayer sample consists of nine alternating layers of Cr and Ni deposited onto a (100) silicon substrate with nominal layer widths of 53 and 66 nm, respectively.[14] Depth profiling was performed by alternating sputter erosion cycles and data acquisition cycles. During the erosion cycles, either the C_{60}^{+} or the Ga^{+} ion beam was operated in dc mode and rastered across an area of 400×400 μm^2. In a data acquisition cycle, sputtered neutral time-of-flight mass spectra of the currently exposed surface were acquired with the same ion source now operating in pulsed mode and rastered across a central crater area of 50×50 μm^2 to minimize disturbances arising from the crater edges.

The measured signal intensity integrated over the ^{58}Ni, ^{52}Cr, and $^{58}Ni^{52}Cr$ peaks in the mass spectrum of sputtered species as a function of the total ion bombardment time is shown in Fig. 1. Erosion with the C_{60}^{+} ion beam clearly resolves all individual layers. Moreover, the apparent depth resolution is maintained without significant degradation throughout the removal of the complete multilayer stack, a total thickness of 529 nm. The NiCr dimer species is only visible in the interfacial regions. These findings are in pronounced contrast with atomic ion erosion where only the first layer is resolved.

As seen in the C_{60}-induced depth profile, the signal intensity from Ni obtained in a Ni layer is about three fold lower than that of Cr obtained in a Cr layer. This effect can be attributed either to a lower sputtering yield or to a lower postionization probability of the Ni atoms. The total sputtering yield of Ni and Cr layers can be calculated from the known layer thickness and the ion fluence needed to profile across an individual layer. The results show that the sputtering yield of Ni (190) is very similar to that of Cr (165) and that the yield induced by C_{60}^{+} is about one order of magnitude higher than that from Ga^{+} ion bombardment (~15). Sputtering yield values are reported as the number of metal

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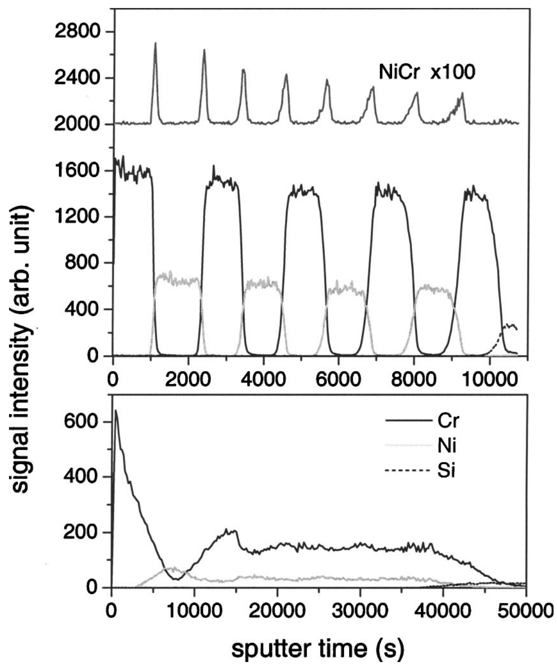

FIG. 1. Integrated signals of neutral atoms vs sputter time for a nine-layer Ni:Cr multilayer stack. The top panel (a) shows the behavior under 15 keV C_{60}^{+} bombardment while the bottom panel (b) shows the response to 15 keV Ga^{+} bombardment. The NiCr signal is displaced upward by 2000 units to enhance visual clarity. The C_{60}^{+} ion current was approximately 0.6 nA into a spot of about 50 microns in diameter. The Ga^{+} ion current was 1.8 nA into a spot of 200 nm. Postionization was achieved using 2.2×10^{13} W/cm^2 laser energy with a pulse width of 100 fs. The laser pulse was repeated at a rate of 1 kHz. Note that the erosion rate is about five times higher for C_{60} bombardment even though the ion current density is nearly three times lower than for the corresponding situation with Ga bombardment, hence the time difference noted.

atoms ejected for each incident C_{60} molecule. Hence, the lower ionization probability of Ni for this fs postionization system is the most likely factor to explain the inherent signal intensity difference between Ni and Cr. The reported sputter yield numbers are consistent with similar values reported from polycrystalline Ag surfaces.[15]

In order to assess depth resolution, sputter time is converted into eroded depth by assuming a constant erosion rate through the complete multilayer stack. Depth scale calibration is performed by setting the sputtering time needed to remove the nominal total thickness of 529 nm to the point where the Si substrate signal has risen to half of its maximum value. The depth resolution is evaluated as the apparent interface width, i.e., the interval between the two points where the Cr and Ni signals reach 16% and 84% of their steady-state values. The depth resolution obtained at the first interface is about 5 nm for ${C_{60}}^{+}$ ions with 15 keV kinetic energy. A similar value is obtained using the full width at half maximum of the NiCr dimer peak observed at each interface. This value is comparable to other Ni:Cr depth-profiling experiments employing low kinetic energy bombardment and sample rotation.[10] Presumably, one reason for this remarkable behavior is that the cluster projectile dissociates upon impact onto the surface, making the behavior of 15 keV C_{60} similar to that of 60 250 eV C atoms. In that sense, the cluster bombardment appears to mimic the use of ultralow-energy atomic primary ion sources, which are known to minimize interlayer mixing effects and thereby provide improved depth resolution.[4–7]

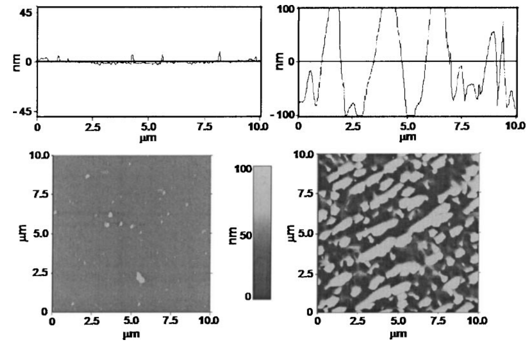

FIG. 2. AFM images of the crater bottom after completion of the depth profile analysis. The left panel (a) shows the image acquired after 15 keV C_{60}^{+} bombardment and the right panel (b) shows the image acquired after 15 keV Ga^{+} bombardment. The rms roughness was calculated using the line scan data shown above the respective images. The rms roughness of the surface before bombardment was about 8 nm.

There is a small mass spectral signal at m/z 12 indicating some possible buildup of carbon in the film due to implantation of carbon atoms associated with C_{60} molecules. It has not been possible to acquire quantitative information from this data since most of the signal arises from photoionization of C-containing gases present in the UHV system. Molecular dynamics computer simulations of Ag{111} bombarded by 20 keV C_{60} molecules[16] suggest that only about 5%–10% of the carbon atoms remain in the film, so we do not expect a high level of carbon implantation.

As mentioned above, it is well known that the depth resolution may be significantly degraded by ion beam-induced topography developing at the bottom of the eroded crater. To investigate this effect, atomic force microscopy (AFM) images of the crater bottom were recorded as shown in Fig. 2. The most interesting observation is that the crater topography induced by C_{60} is much less pronounced than that generated by atomic projectiles. For example, a 15 keV ${C_{60}}^{+}$ bombardment induces a root-mean-square (rms) roughness of 2.5 nm, whereas the corresponding value under Ga^{+} bombardment is about 100 nm. This finding suggests that the large degradation of depth resolution observed with Ga^{+} projectiles is mostly due to ion beam-induced topography evolution. The same observation has been made earlier for other atomic projectiles of different kinetic energies.[10]

The crystalline structure of the bombarded surface appears to be of only minor importance under cluster bombardment, whereas it has a significant influence on the sputtering yield produced by atomic projectiles. For example, the rms roughness for 3 keV bombardment of a Ni:Cr stack by ${O_2}^{+}$ and ${SF_5}^{+}$ yields values of 65 nm and 10 nm, respectively,[17] indicating that the effect becomes less pronounced with increasing size of the projectile cluster.

The strong inhibition of topography observed here appears to be unique to C_{60} projectiles. This result is qualitatively supported by molecular dynamics computer simulations comparing the collision cascades induced by C_{60} and Ga, respectively, which indicate that under C_{60} bombardment most of the sputtered flux is ejected from a completely amorphized surface region.[16] The simulations also show that C_{60} has a shorter penetration depth and causes less interlayer mixing than other projectiles. On the other hand, the simulations indicate that the average escape depth of sputtered particles and, hence, the intrinsic depth resolution, is increased for C_{60} bombardment. These calculations suggest that up to four atomic layers contribute to the measured signal, a finding which would lead to an intrinsic depth resolution of about 1 nm.

In conclusion, we demonstrate that the use of a C_{60}^+ primary ion source offers significant advantages over the other known ion sources employed for sputter depth profiling, including improved depth resolution and faster erosion rates. These advantages are attributed to the higher sputtering yield, less interlayer mixing, and much less crater topography resulting from C_{60}^+ bombardment. The depth resolution achieved here with a relatively high kinetic impact energy of 15 keV is comparable to values reported using low-energy atomic primary ion sources and sample rotation to minimize ion bombardment-induced roughness. Although the reported time to etch through the full 529 nm film is nearly 3 h, it should be noted that by reducing the analysis area from 400×400 microns to 100×100 microns, this time can be reduced to less than 12 min.

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