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INTERFACE STRUCTURE AND STABILITY IN Ti/C SUPERLATTICES

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ABSTRACT

We have performed a coordinated experimental and theoretical investigation of the structure and stability of Ti/C multilayers. The samples were prepared by conventional techniques and the lattice structure was characterized by X-ray diffraction. Electron Energy Loss and Auger spectroscopies (EELS,AS), in conjunction with Rutherford Backscattering (RBS) were employed to characterize the chemical composition of the samples. It was observed that the Ti/C interface is isolated by a thin titanium oxide layer. The center of the Ti layer gives a typical EELS spectrum of Ti metal. The carbon shows a graphitic character. We have used total energy calculations to study the crystallographic structure and electronic behavior at the interface in Ti-C superlattices. This involved examining a series of structures in the Ti-C system proceeding from the ground state NaCl structure to superlattices. In particular we performed total energy calculations for an arrangement of atoms designed to allow direct investigation of the competition between Ti-C bonds and C-C bonds. We conclude that the equilibrium structure is dominated by C-C bonding and so we find that the interface has a graphite like atomic arrangement rather than a carbide like arrangement. We than further explored the interactions in this graphitic arrangement and found that the interface does not have a significant Ti-C bonding and that the interface most likely consists of simply a layer of graphite adjoining a titanium surface. This carries important implications for the diffusion and bonding at the interface.

The multilayers studied in the present paper were prepared using a Perkin-Elmer argon plasma rf-sputter deposition system. The substrates placed on a water cooled platform rotate below the carbon (reactor-grade ATJ graphite) or Ti(99.95%) targets. A shutter with a circular opening allows the preparation of several samples under almost identical conditions. Typical base pressures were 5x10-5 Pa and the argon pressure during deposition (0.15PA) was controlled using a capacitance manometer at argon gas flow rates of 0.4 cc/sec. The argon gas flow passed through a titanium gettering system. The silicon single crystals were micropolished and heat treated prior to depositions. Samples were deposited at typical rates of 52 A/min for Ti and 16 A/min for carbon at an 8 cm target-substrate distance. The samples were characterized using Microcleavage Transmission Electron Microscopy[1] and X-ray diffraction. The large number of peaks and their respective intensities were characteristic of well prepared samples[2,3]. Table 1 gives the list of samples studied in this work.

TABLE I. Ti and C composition of the multilayers

Ti Thickness	C Thickness	No. of Periods
37.6A	32.0A	50
20.6A	8.8A	50
25.6A	10.2A	50
27.0A	41.0A	65
20.2A	4.7A	50

We employed EELS to study the sample composition as a function of depth. This was possible by varying the electron primary energy, which allows scanning down to about 100A below the surface. We used standard samples to identify the different energy loss peaks. The oxidation state of titanium was identified by measuring the 3p spin-orbit splitting. We want to emphasize that this technique shows a much better sensitivity than AS for chemical composition identification. If one uses mild sputtering conditions for very short times, the depth analysis can be extended by about 50A more.

We used RBS to obtain the elemental composition of the sample as a function of depth. Two different ion beams were employed in this investigation, protons and alpha particles. The measurements were performed using the Brooklyn College Dynamitron accelerator. The AS and EELS measurements were preformed in an UHV chamber, using Ti(100) and Ti(111) as standards. Carburization of the titanium metal surface was performed to obtain the carbide.

The AS spectra for all multilayers show the presence of a prominent carbon peak which has graphitic character. After mild sputtering (~1 min), and depending on the thickness of the sample, one started to observe oxygen and titanium peaks. Increased sputtering time or current produced undesirable mixing of the C and Ti layers. The EELS spectra gave

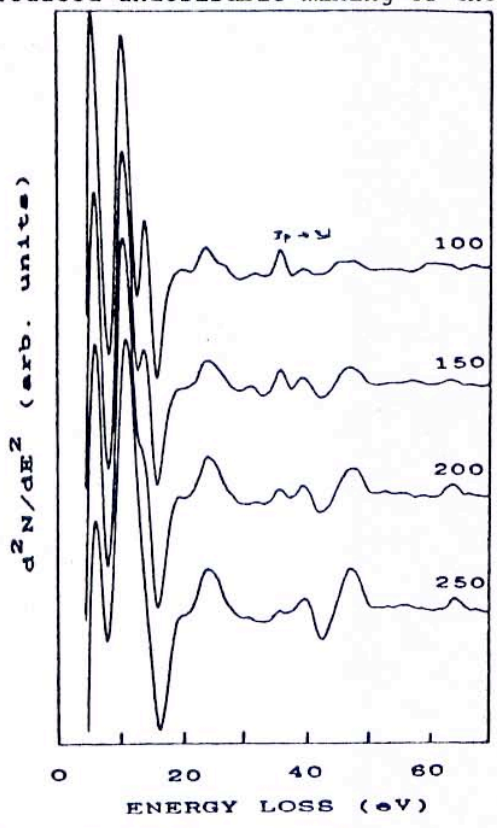

Figure 1 EELS spectra for primary energies between 100 and 250 eV.

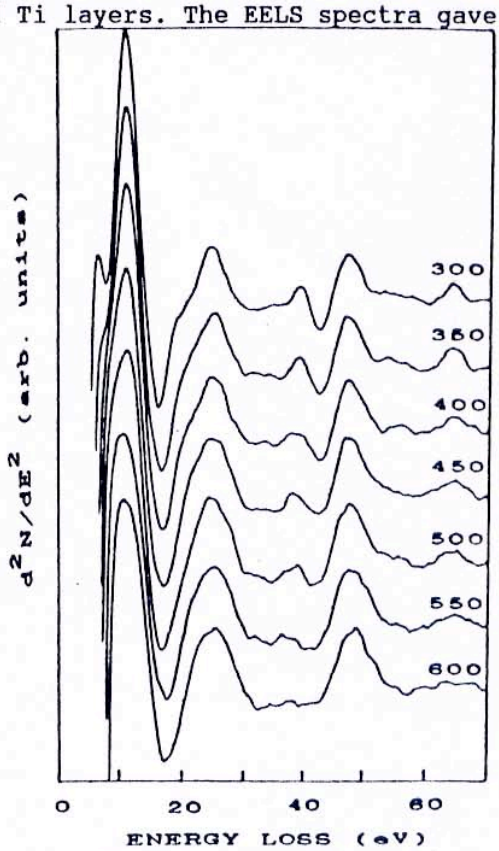

Figure 2 EELS spectra for primary energies between 300 and 600 eV.

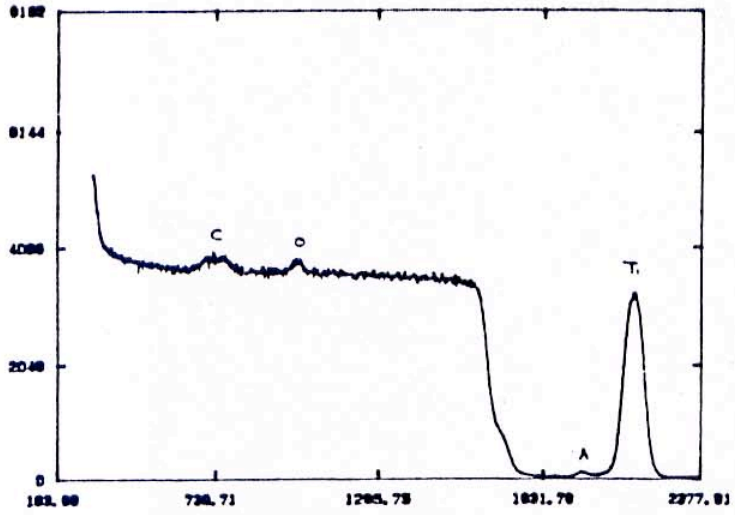

Figure 3 RBS spectrum for alpha particles at 3.05 MeV

a more detailed profile of the chemical composition of the sample. The top layer of carbon was graphitic. At the interface titanium oxide was present. Figures 1 and 2 show a selected number of spectra for a C=8.8A and Ti=20.6A sample; similar spectra were obtained for the other samples. We observed the presence of a thin oxide layer, easily characterized by three prominent interband transitions below 20 eV and the core 3p ionization losses. When the primary energy is above 250 eV the EELS spectrum is dominated by Ti metal features (plasmon peak at 26 eV, different 3p energy). The estimated thickness of the oxide layer is 4-5A. EELS alone is not enough to detect the presence of O in the bulk of the sample. In order to detect the presence of oxygen in the bulk of the sample we used the elastic scattering resonance of alpha particles at 3.05 MeV. For all the samples we observed the presence of two peaks due to Ti and C as well as features due to the substrate. Figure 3 shows a to the substrate. Figure 3 shows a typical spectrum at the resonance energy for alpha particles. We also observed a small peak below the Ti that corresponds to argon. There is a strong dependence of the O peak on the alpha particles energy. A work of caution is necessary concerning the areas of the peaks. Although O and C peaks seem to have similar areas, the amount of oxygen is very small, about 1-2%. The fact that we have this amount of oxygen in the sample is consistent with the presence of the oxide interfaces throughout the sample. We also observed considerable radiation damage of the sample after several hours irradiation.

We have used total energy calculations to study the crystallographic structure and electronic behavior at the interface in Ti-C superlattices. This involved examining a series of structures in the Ti-C (and to a lesser extent, W-C) system proceeding from the ground state NaCl structure to superlattices. In particular we perform total energy calculations for an arrangement of atoms designed to allow direct investigation of the competition between Ti-C bonds and C-C bonds. We conclude that the equilibrium structure is dominated by C-C bonding and so we find that the interface has a graphite like atomic arrangement rather than a carbide like arrangement. We then further explore the interactions in this graphitic arrangement and find that the interface does not have significant Ti-C bonding and that the interface most likely consists of simply a layer of graphite adjoining a titanium surface. Since the series IV transition metal carbides are least susceptible to graphite formation, this is presumably the case for all other transition metal-carbon superlattices. This carries important implications for the diffusion and bonding at the interface. These total energy calculations

have been completed using a recently developed self-consistent linear combination of muffin tin orbitals electronic structure method. This is a full-potential, all-electron, variation on standard LMTO electronic structure methods and, along with careful self-consistent determination of the parameters involved, allows accurate total energy calculations of the type of low symmetry systems involved in this study.

In summary, we have experimentally observed the formation of a thin titanium oxide layer at the carbon-titanium interface. The titanium layers have a bulk metal character, the carbon layers show a graphitic behavior. These results are in very good agreement with the theoretical calculations using the full-potential LMTO technique.

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