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MAX-PHASES INVESTIGATED BY SOFT X-RAY EMISSION SPECTROSCOPY

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ABSTRACT

The electronic structures of the MAX-phases Ti_3AlC_2, Ti_3SiC_2 and Ti_3GeC_2 were investigated by soft X-ray emission spectroscopy. These nanolaminated carbide compounds represent a class of layered materials with a combination of properties from both metals and ceramics. The bulk-sensitive soft X-ray emission technique is shown to be particularly useful for detecting detailed electronic structure information about internal monolayers and interfaces. A weak covalent Ti-Al bond is manifested by a pronounced shoulder in the Ti L-emission of Ti_3AlC_2. When Al is replaced by Si or Ge, the shoulder disappears. Furthermore, the spectral shapes of Al, Si and Ge in the MAX-phases are strongly modified in comparison to the corresponding pure elements. By varying the constituting elements, a change of the electron population is achieved causing a change of covalent bonding between the laminated layers, which enables control of the macroscopic properties of the material.

INTRODUCTION

In the last few years, the interest in ternary carbides and nitrides, so-called $M_{n+1}AX_n$-phases has grown significantly both from a scientific and a technological point of view [1]. Generally, there are three different kinds of crystal structures of these materials, often denoted 211, 312 and 413, corresponding to n=1, 2 and 3. The letter M denotes an early transition metal, A is an element in the groups IIIA and IVA and X is either carbon or nitrogen. The MAX-phases exhibit a unique combination of metallic and ceramic properties, including high strength and stiffness at high temperature, resistance to oxidation and thermal shock, and display high electrical and thermal conductivity [1]. The unique macroscopic properties of the MAX-phases are related to the underlying nanolaminated crystal structure, the electronic structure and the chemical bonding of the individual atomic layers. For the 312-crystal structure, there are three different carbides, Ti_3AlC_2, Ti_3SiC_2 and Ti_3GeC_2. Sintered bulk MAX-compounds are useful in many technological high-temperature applications such as heating elements in ovens. In other applications where e.g., low-friction properties are useful, high-quality thin film coatings of MAX-phases are utilized.

In this paper, soft X-ray emission (SXE) spectroscopy was applied to probe the partial electronic structures of Ti_3AlC_2, Ti_3SiC_2 and Ti_3GeC_2. The photon-in-photon-out SXE spectroscopic technique is element selective and more bulk sensitive than electron-based techniques such as X-ray absorption and X-ray photoemission spectroscopy [2-4]. This makes it possible to obtain information about the buried internal monolayers and interfaces in the compounds. Each element in the MAX-phase compounds was probed separately and the partial electronic structures of the valence bands were projected through the dipole transition selection rules.

EXPERIMENT

The SXE measurements were performed at the undulator beamline I511-3 at MAX II (MAX-lab National Laboratory, Lund University, Sweden), which includes a 49-pole undulator and a modified SX-700 plane grating monochromator [5]. The SXE spectra were recorded with a high-resolution Rowland-mount grazing-incidence grating spectrometer [6] with a two-dimensional detector. The Ti L and C K X-ray emission spectra were recorded using a spherical grating with 1200 lines/mm of 5 m radius in the first order of diffraction. The Al L, Si L and Ge M spectra were recorded using a grating with 300 lines/mm, 3 m radius in the first order of diffraction. During the SXE measurements at the Ti $2p$, C $1s$, Al $2p$, Si $2p$ and Ge $3p$ edges, the resolutions of the beamline monochromator were 1.6, 1.0, 0.3, 0.2, and 0.4 eV, respectively. The SXE spectra were recorded with spectrometer resolutions 0.7, 0.2, 0.2, 0.2, 0.2 eV, respectively. The measurements were performed with a base pressure lower than 5×10^{-9} Torr. In order to minimize self-absorption effects [7], the angle of incidence was 30 degrees from the surface plane during the emission measurements. The X-ray photons were detected parallel to the polarization vector of the incoming beam in order to minimize elastic scattering. The deposition procedure of the epitaxially grown thin film coatings are described elsewhere [8].

RESULTS AND DISCUSSION

Figure 1 shows a set of soft X-ray emission spectra excited nonresonantly above the Ti $L_{2,3}$, C K, Al $L_{2,3}$, Si $L_{2,3}$ and Ge $M_{2,3}$ edges for Ti_3AlC_2, Ti_3SiC_2 and Ti_3GeC_2. The excitation energies were 477 eV, 310 eV, 120 eV, 120 eV and 165 eV, respectively. For comparison, the spectra are normalized to unity and plotted on a common photon energy scale relative to the Fermi level (E_F) using core level XPS binding energies for the same type of compounds available in the literature [3,4]. For Ti $2p_{3/2}$, C $1s$, Si $2p$, Al $2p$, and Ge $3p_{1/2}$, 454.7 eV, 281.83 eV, 99.52 eV [3], 71.9 eV [4] and 125.5 eV [8] binding energies were used, respectively.

In the Ti L_{23} spectra at the top of Fig. 1, the main L_3 and L_2 emission lines dominated by $3d$ final states are observed at –2.5 eV and 3.7 eV and the intensity of the L_3 emission line is about 6 times higher than the L_2 intensity. The measured peak splitting due to the spin-orbit interaction is thus 6.2 eV. Notably, a broad peak structure is also observed at –10 eV in all three Ti $L_{2,3}$ spectra. This structure is not observed in Ti $L_{2,3}$ spectra of pure Ti [9] and can therefore be attributed to hybridization with carbon. The arrow at the top of Fig. 1 indicates the most significant difference between the three systems, namely the pronounced shoulder in the Ti_3AlC_2 system. The peak splitting between the shoulder and the main line is 1.5 eV. The shoulder clearly originates from hybridization with Al in Ti_3AlC_2, an interpretation that is also consistent with bandstructure calculations [8,10].

In the C K spectra, the main peak is found at –2.6 eV and there are shoulders on both the low- and high-energy sides of the main peak at –4.2 eV and –2 eV. The main peak and the shoulder correspond to the occupied C $2p$ orbitals hybridized with the Ti $3d$ bonding and antibonding orbitals of the valence bands [8]. Note that the three C K spectra have very similar spectral shapes. This suggests that the interaction between the C and A atoms is very small.

The Al $L_{2,3}$ spectrum of Ti_3AlC_2, has the main peak at –3.9 eV and is dominated by $3s$ final states. Al $3p$ states dominate close to E_F but are dipole forbidden at the $2p$ edges and do not
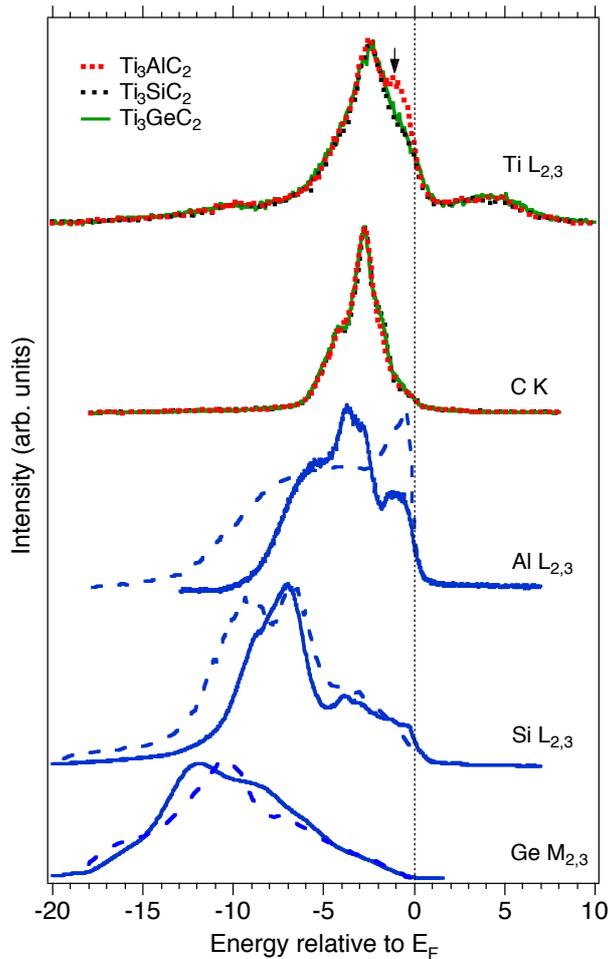
Figure 1: (Color) Ti *L*, C *K*, Al *L*, Si *L* and Ge *M* X-ray emission spectra of the MAX-phases Ti_3AlC_2, Ti_3SiC_2 and Ti_3GeC_2. The excitations were made nonresonantly at 477 eV, 310 eV, 120 eV, 120 eV and 165 eV, respectively. The spectra were aligned on a common energy scale relative to the Fermi level (E_F) by using core-level XPS binding energies [3,4] (454.7 eV, 281.83 eV, 71.9 eV, 99.52 eV, and 125.5 eV, respectively). The measured spectral profiles of Al, Si and Ge are compared to spectra of the pure elements from Refs. [11, 13, 15] (dashed lines). The Ge spectrum (bottom) was smoothed with a binomial average of the raw data.

contribute to the spectrum. The spectral profile of Al in Ti_3AlC_2 also differ substantially from spectra of pure Al metal which has a sharp and dominating peak structure close to E_F [11]. A similar spectral profile as in Al of Ti_3AlC_2 has been observed in the metal aluminides [12].

The Si $L_{2,3}$ spectrum of Ti_3SiC_2, is dominated by a peak structure at –7 eV, at significantly lower energy than in Al. The lower energy of the main structure in Si is related to the extra valence electron in Si in comparison to Al. As in the case of Al, the Si $L_{2,3}$ spectrum is dominated by *3s* final states and the Si *3p* states are dipole forbidden. The spectral profile of Si in Ti_3SiC_2 also largely differs from spectra of pure Si, which has a pronounced double structure [13]. The spectral shape of Si in Ti_3SiC_2 is similar to the metal silicides [14].

As shown at the bottom of Fig. 1, the Ge $M_{2,3}$ emission spectrum of Ti_3GeC_2 is dominated by a double structure with peaks at –12 and –8 eV. These peaks are due to the M_3 and M_2 emission lines. The measured $M_{2,3}$ emission of the *4s* valence band of Ge in Ti_3GeC_2 is about two orders of magnitude weaker than the Al $L_{2,3}$ emission in Ti_3AlC_2 and the Si $L_{2,3}$ emission in Ti_3SiC_2 and for comparison of the spectral profiles the raw data of Ge was smoothed in figure 1. The double structure observed in the

Ge $M_{2,3}$ emission spectrum of Ti_3GeC_2 is significantly different from the triple-peak structure in Ge $M_{2,3}$ emission of pure Ge [15]. As in the case of Si, the spectral shape of Ge in Ti_3GeC_2 is similar to the metal germanides [16].

A comparison between the spectral profiles of measured MAX-phases and electronic structure calculations including core-to-valence dipole transition matrix elements is presented elsewhere [8] yielding a qualitative agreement in the interpretation between experiment and theory.

CONCLUSION

Soft X-ray emission spectra of the MAX-phases Ti_3AlC_2, Ti_3SiC_2 and Ti_3GeC_2 are presented. The most significant difference between the three compounds is a double structure in the Ti $L_{2,3}$ emission of Ti_3AlC_2. This is related to the fact that the Ti-Al bonding displays less covalent character than the Ti-Si and Ti-Ge bonds. The X-ray emission spectral profiles of Al in Ti_3AlC_2, Si in Ti_3SiC_2 and Ge in Ti_3GeC_2 are found to be very different in comparison to the corresponding pure elements. These strongly modified spectral structures are due to significant hybridization with the surrounding Ti and C. By replacing Al with the isoelectronic Si and Ge elements, the achieved change in the valence electron population and thus the modified chemical bonding implies a change of the macroscopic material properties.

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