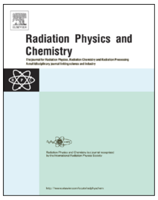
Radiation Physics and Chemistry 93 (2013) 168–173

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



Complementary characterization of Ti–Si–C films by x-ray diffraction and absorption

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HIGHLIGHTS

- Films T-iSi-C were grown by magnetron sputtering from three targets with different power.
- The comprehensive characterization by XRD and XAS was performed.
- Procedures to achieve the stoichiometry leading to the Ti_3SiC_2 phase was proposed.

ARTICLE INFO

Article history:
Received 13 August 2012
Accepted 26 February 2013
Available online 14 March 2013

Keywords:
X-ray diffraction
X-ray absorption
MAX phases
Thin layers
Co-sputtering
Ordering

ABSTRACT

Advanced electronic devices based on III-N semiconductors, particularly these operated at the high power and high frequency or corrosive atmosphere, need elaboration of new technology for contacts metallization which are thermally and chemically stable. Performed studies aimed at the development of materials for applications in the improved metallization. Due to the unique combination of the metallic electro-thermal conductivity and ceramic resistance to oxidation and thermal stability, the MAX phases were chosen as the materials potentially applicable to this task. Particular interest lies in the MAX phases based on the Ti, Si and C or N atoms, especially on the Ti_3SiC_2 phase. The paper focuses on a comprehensive characterization of films grown by means of high-temperature magnetron Ti, Si and C co-sputtering. The complementary characterization by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) is presented.

XRD studies pointed out the presence of several phases in the investigated samples, therefore XAS as an atomic sensitive probe was applied to examine the average atomic order around Ti atoms as a function of the technological parameters and to point towards proper procedures to achieve the appropriate stoichiometry around Ti atoms and finally the Ti_3SiC_2 phase.

1. Introduction

In recent years significant research efforts have been focused on materials suitable for implementation in the development of high frequency and high power electronic devices, in particular the ones based on group III nitrides. As these materials are semiconductors with a wide band gap, they are well suited for operation under high electric bias, in harsh conditions and at elevated temperatures, which arise both from the potential work environment as well as from the internal heat dissipation due to the high power operation. Such operation conditions lead to a fast degradation of the common electric contacts metallization on these devices and require that thermally stable materials are applied in such metallization. The so called MAX phases, due to their properties, are potentially applicable in these kind of devices. On one hand they exhibit the properties of metals, showing good thermal and electrical conductivity, machinability, high hardness (Lin et al., 1994). On the other hand they have ceramic properties with damage tolerance, oxidation resistance, and thermal stability even at temperatures as high as 1000 °C (Barsoum, 2000; Emmerlich et al., 2007). These particular properties are related to the nanolaminate structure of this class of compounds (Jeitschko et al., 1963; Emmerlich et al., 2007, Palmquist et al., 2004). The chemical formula of the phases is $M_{n+1}AX_n$ ($n=1, 2, 3$), where M stands for transition metal, A for an element from group IIIA or IVA and X for carbon or nitrogen. A monocrystalline MAX phase consists of MX monolayers intertwined with monoatomic A layers. Fig. 1 shows the unit cell of $M_{n+1}AX_n$ phases for $n=2$.

Among the M_3AX_2 phases very promising for applications in metallization to III-N compounds is the Ti_3SiC_2 phase (Eklund

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http://dx.doi.org/10.1016/j.radphyschem.2013.02.037

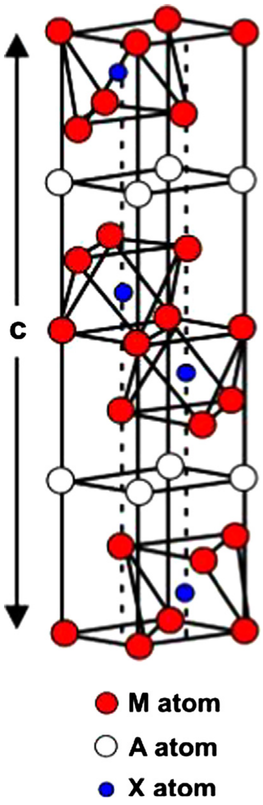

Fig. 1. Unit cell for a M_3AX_2 phase (Ti_3SiC_2).

et al., 2007; Högberg et al., 2005). The Ti_3SiC_2 structure has been reported by Jeitschko, Nowotny (1967) as hexagonal in space group *P*63/*mmc* with $a < 3.07$ Å and $c < 17.69$ Å. The Ti occupies 2a and 4f sites, Si a 2b site and C a 4f site (Wyckoff positions) and the structure exhibits two polymorphs in which Si shifts to 2d in higher temperature. As shown in Fig. 1, the phase consists of a layered structure with a double Ti–C block, each made of two edge-sharing CTi_6 octahedra. A square-planar Si plane separates the double Ti–C blocks what is crucial for the physical properties of the phase but it has been shown (Palmquist et al., 2004) that it is very easy to modify the stacking sequence of Si layers in the *MAX* film during growth therefore it is difficult to produce the Ti_3SiC_2 phase with proper stoichiometry and good crystalline structure. This compound is the most studied among the MAX phases and the majority of reports focus on the mechanical properties of high temperature sintered bulk material (El-Raghy et al., 1999; Sarkar et al., 2005; Wu et al., 2010; Sun et al., 2005), however recently Emmerlich et al. (2004) showed that it is possible to fabricate thin monocrystalline films of Ti_3SiC_2 through magnetron sputtering. As sputtering is a technique compatible with electronic device fabrication, this enabled the MAX phases to be considered for applications in electric contact metallization. In the presented paper the attempts to grow thin and monocrystalline films of the Ti_3SiC_2 phase by means of high-temperature magnetron sputtering from three independent cathodes are reported and the problems with achieving the stoichiometric phase are discussed and solution is proposed. The structural characterization of the deposited films was carried out by means of X-ray diffraction (XRD). Phase identification did not lead to a conclusive recognition of the Ti_3SiC_2 phase in any of the samples. We demonstrate that in such a case the constructive conclusions for technology can be provided by the XAS studies. In the first step the Extended X-Ray Absorption Spectroscopy (EXAFS) studies were performed for one set of samples and suggestions for the changes in the technology were given. According to them second set of samples was produced with stoichiometry very close to the Ti_3SiC_2 compound.

2. Experiment

Thin Ti–Si–C films were deposited onto Al_2O_3(00.1) substrates by means of high temperature magnetron sputtering from elemental (5N) Ti, Si and C targets in Ar atmosphere using a Surrey NanoSystems γ1000C reactor. The procedure was different from that used by Palmquist et al. (2002) where C_{60} was used as carbon source and deposition was performed on MgO substrate. With three individual targets, it is possible to vary the content of each element in the deposited films by changing the power at each target in order to reach the Ti_3SiC_2 stoichiometry. The proper chose of the power depend on the reactor geometry and type and is not an easy task. In the analyzed samples the power at the Ti target was kept at 70 W and the powers at Si and C targets were changed. The numbers given together with each sample name (e.g. 70/70/180 W) denote the power at Ti, Si and C target, respectively. Prior to deposition the substrates were properly cleaned. The deposition was performed in two steps. First, the substrate was heated up to 850 °C and a thin seed layer of ~15 nm TiC_x was deposited from Ti and C targets with the power indicated for given sample. Subsequently, the temperature was raised to 900 °C and the Si target was switched on with indicated power and ~150 nm thick Ti–Si–C film was deposited. The sample with TiC_x layer (C16) deposited on the Al_2O_3(00.1) substrate was examined as a reference for buffer layer. The power at the C target for this sample was 212 W. Two sets of samples were prepared. One with high power at the Si target and medium at C target. The second set of samples was grown under the same conditions but the power at the targets was changed in accordance with the results from the EXAFS analysis of the first set of samples and was set lower at the Si target and higher at the C target.

The XRD measurements were performed using the X'Pert, PRO MPD in Bragg–Brentano configuration, equipped with Cu X-ray tube in the 2θ angle range from 30° to 100°. The Ti K edge measurements were done at HASYLAB A1 station. Fluorescence mode of detection at LN temperature was used. The samples were sufficiently thin to avoid the self-absorption effect in the registered signal. A commercial powder of TiC was used as a reference to adjust some parameters for EXAFS analysis. The spectra for the TiC powder were collected in the transmission detection mode. Fitting procedures has been executed using Athena and Artemis programs (Ravel and Newville, 2005). Theoretical amplitudes and phases were calculated by FEFF8.4. (Zabinsky et al., 1995; Akundinov et al., 1998). The most important scattering paths were considered and compared with references.

3. Results and discussion

X-ray diffraction patterns, measured for all samples in the wide range of 2θ angles, did not reveal the Ti_3SiC_2 phase. The low angles parts of these patterns for the first set of samples and *C*16 buffer layer are shown in Fig. 2. In this range of angles two reflections: 00.8 and 10.5 from the Ti_3SiC_2 phase (the database positions of these reflections are marked in Fig. 2) should be observed in the vicinity of Al_2O_3 00.6 substrate reflection. For the chosen substrate orientation the 00.8 reflection related to the (00.1) lattice plane should be preferred (Palmquist et al., 2004). In none of the samples the sharp peak at the position of this reflection was observed. In the case of *C*117 (70/110/148 W) sample, the very broad diffraction maximum at the position of 00.8 Ti_3SiC_2 phase was detected. In the *C*111(70/85/158 W) sample pattern