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Ti_3SiC_2-formation during Ti-C-Si multilayer deposition by magnetron sputtering at 650 °C

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Ti_3SiC_2 films were deposited from three separate magnetrons with elemental targets onto Si wafer substrates. The substrate was moved in a circular motion such that the substrate faces each magnetron in turn and only one atomic species (Ti, Si or C) is deposited at a time. This allows layer-by-layer film deposition. Material composition was determined by energy dispersive X-Ray (EDX). High resolution transmission electron microscopy (HRTEM) and Raman spectroscopy were used to gain insights into thin film atomic structure arrangements. Using this new deposition technique, at a deposition temperature of 650 ^{0}C formation of Ti_3SiC_2 MAX phase was obtained, while at lower temperatures phase separation is observed and only silicides and carbides are formed. Significant sharpening of Raman E_{2g} and A_g peaks associated with Ti_3SiC_2 formation was observed.

Keywords: MAX phase, titanium silicon carbide, nano-laminate, Physical Vapour Deposition, Raman microscopy, phase separation

Highlights:

1. Physical Vapour Deposition in layer-by-layer magnetron deposition system of Ti_3SiC_2 composition was performed on silicon wafer substrates with native oxide
2. At comparatively low substrate temperature of 650 ^{0}C Ti_3SiC_2 MAX phase was formed
3. At temperatures below 650 ^{0}C formation of binary phases was observed
4. Raman spectra from Ti_3SiC_2 composition allows MAX phase identification and separation from binary compounds by sharp E_{2g} and A_g peaks in the 500-750 cm^{-1} region.

In the 1960s and 1970s Nowotny and co-workers succeeded in bulk synthesis of a large class of ternary carbides and nitrides [1, 2]. One of those materials, namely Ti_3SiC_2, was also synthesised at the time by Chemical Vapour Deposition [3, 4] The renaissance in the last decade is closely linked to Barsoum's early work [5] and later reviews [6-9]. The general formula of the materials is $M_{n+1}AX_n$, where n=1, 2, or 3 and M is a transition metal, A is an A-group element, and X is C and/or N. The name "MAX phases" was coined by Barsoum [6]. Bulk MAX phases in general require high, in excess of 1200 ^{0}C, temperature for synthesis and synthesis of pure phases is nontrivial because of competing binary compounds. First synthesis by Physical Vapour Deposition was reported in 2002 by Palmquist *et al.* onto single-crystal substrates [10]. In excess of 60 compounds have been synthesised up to date [8, 9].

Retention of mechanical and oxidation resistance of MAX phases at temperatures above 1000 ^{0}C made synthesis of thin film MAX phase materials very relevant. An outstanding research topic is to reduce the formation temperature of MAX phases. For the 211 phases Cr_2AlC, V_2AlC, Cr_2GeC, and V_2GeC it is possible to form fully developed crystalline structures at around 500-700 ^{0}C [11-17]. The Ti-containing 211 phases Ti_2AlC and Ti_2GeC, however, were grown at temperatures near higher bracket (~700 °C) [18, 19].

For the 312 phases with longer c-axes, for instance for the most studied Ti_3SiC_2 phase, film growth of crystalline material on epitaxial substrates typically requires temperatures around 900 ^{0}C, see for example [20]. Larger unit cells require more thermal activation, due to the longer diffusion length compared to smaller unit cells. Application of the Ti_3SiC_2 thin films can be significantly widened if the synthesis temperature can be further reduced to below the 700 ^{0}C region. Emmerlich [19] obtained Ti_3SiC_2 by reactive magnetron co-sputtering from three elemental targets at 750 °C, however, with competitive TiC_y growth.

We report creation of Ti_3SiC_2 MAX phase on silicon with native oxide (non-epitaxial) substrate at 650 ^{0}C using new method of elemental layer-by-layer-deposition. The schematic diagram of the deposition system is shown in Fig.1.

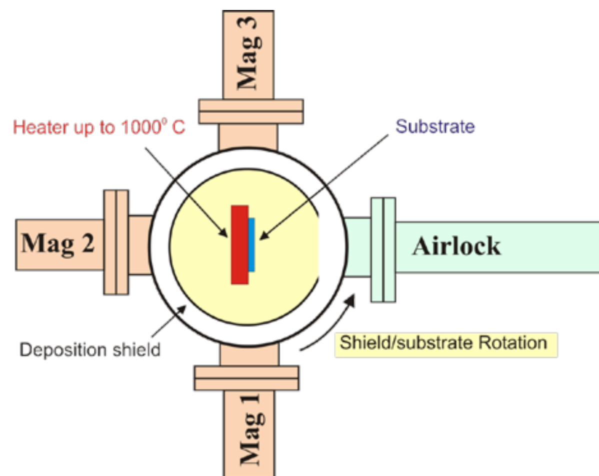

Fig. 1. Schematic diagram of the deposition system

Three 2.5-inch magnetrons with elemental Ti, Si, and C targets were placed around the central volume of the deposition chamber. The Si (100) substrate with native oxide was placed into the heater and inside deposition shield facing a window. All central assembly can be continuously rotated with a constant speed so that the substrate sequentially faces magnetrons and Ti, Si, and C are deposited. The thickness of deposited layers is determined

by individual element fluxes and speed of rotation which dictates how long the substrate can see individual magnetrons.

The samples were loaded through an airlock system and the base pressure in the chamber was at around 1×10^{-5} Pa. During deposition Ar partial pressure was at around 0.6 Pa as measured by a Penning gauge without corrected sensitivity. The deposited samples have atomic composition close to stoichiometric Ti_3SiC_2 as accessed by energy dispersive X-ray spectroscopy (EDX). Samples presented in the communication were deposited at a speed of 0.53 nm/turn.

X-Ray Diffraction (XRD) spectra for a sample deposited at 610 ^{0}C are shown in Fig. 2. Present are X-ray line positions for the compounds TiC, Ti_3SiC_2, and possibly $Ti_5Si_3(C_x)$. However, there is complicated overlapping line structure especially between 30 and 45^0. High-resolution TEM was performed in order to support the phase identification.

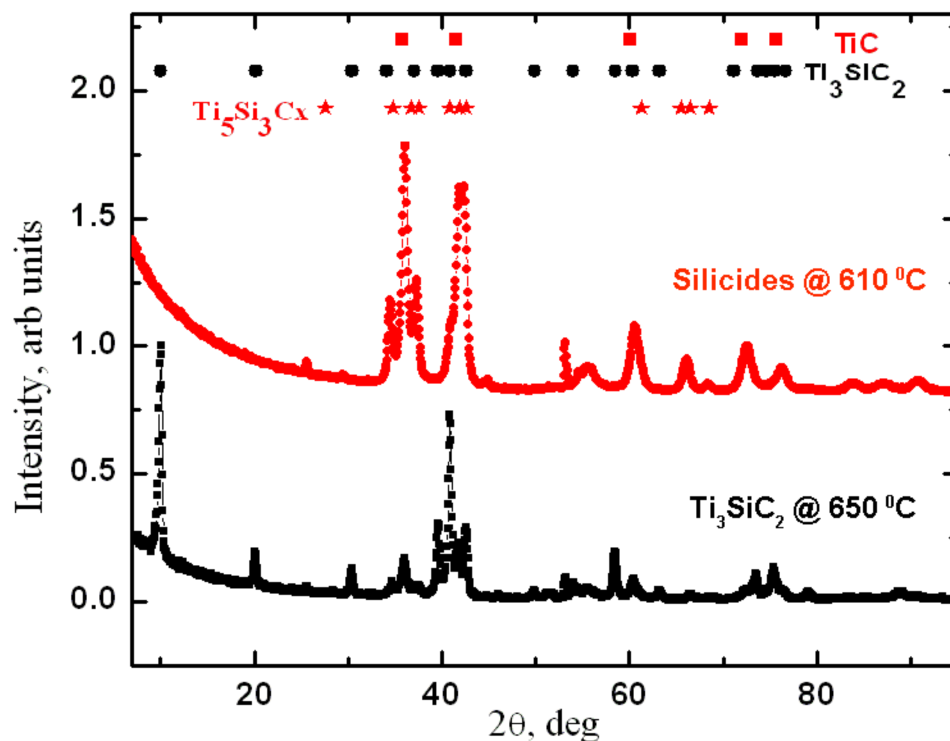

Fig.2. XRD spectra for samples deposited at 610 and 650 ^{0}C. XRD line positions for TiC (red squares), Ti_3SiC_2 (black circles) and $Ti_5Si_3C_x$ (red stars) are shown at the top of the drawing.

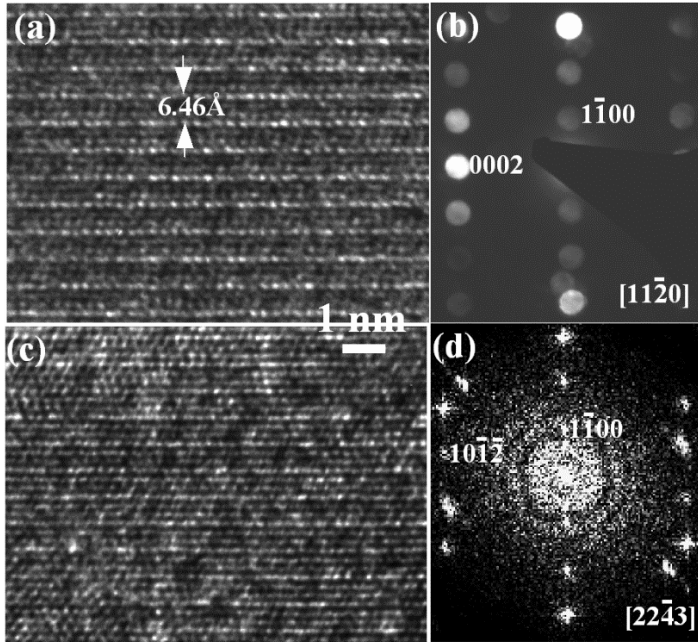

Fig.3. Lattice images in (a) [11-20] and (c) [22-43] zone axes with corresponding (b) selected area diffraction pattern and (d) fast Fourier transform, respectively, from the sample deposited at 610 ^{0}C.

Selected area electron diffraction data in the [11-20] and [22-43] zone axes in Fig 3 (b) and (c), respectively, reveals Ti_5Si_3 material with a dissolved carbon. The structure can be described as $Ti_5Si_3(C_x)$. The Ti_5Si_3 was probably first discussed by Svechnikov *et al* [21] and lately with added carbon in [22-25]. The Ti_5Si_3 crystal structure is hexagonal [22] and can dissolve up to 11 at.% of carbon. The 6.46 Å marked in (a) corresponds to the d-spacing of (1-100) planes. The formation of this phase at a substrate temperature of 610 °C is expected and is in line with previous results on the Ti-Si-C system [25, 26]

As temperature of the substrate rises to 650 ^{0}C, the formation of Ti_3SiC_2 is observed both by XRD and TEM (see Fig. 4). It is evident from XRD data that some TiC_x is still present, but the film is dominated by Ti_3SiC_2. The temperature of 650 ^{0}C is significantly different from synthesis at 750 ^{0}C by co-deposition from elemental targets [26]. The reason for this is layer-by-layer (element-by-element) deposition in the current work. It is also likely related to the small diffusion lengths for Ti, Si, and C to partition over the growth surface of the Ti_3SiC_2 film for such 312 MAX phase grains to outgrow competing TiCx and 53x compounds. The 312 MAX phase grains formed on Si with the native oxide and this shows that at the right growing conditions MAX phases can be in principle formed on non-epitaxial substrates.

Raman spectra acquired at 514.3 nm excitation (Renishaw inVia micro Raman, backscattering geometry) reveal transition from silicides to MAX phases as substrate temperature increase from 610 to 650 ^{0}C. While whole set of peaks undergoes changes in position and intensity, the more notable is the rise in intensity of two components in the region of 600 cm^{-1}. According to the previous work and modelling [27] the components can be assigned to carbon oscillations with symmetry E_{2g} (622 cm^{-1}) and A_g (657 cm^{-1}) in the Ti_3SiC_2 crystal structure [28].

In conclusion, thin film MAX phase Ti_3SiC_2 on silicon substrate has been deposited at substrate temperature 650 ^{0}C during sequential deposition of three Ti, one Si, and two C

atoms. Raman spectra can be used for fast identification of Ti_3SiC_2 as Raman peaks in the 600 cm^{-1} region sharpens significantly for MAX phase.

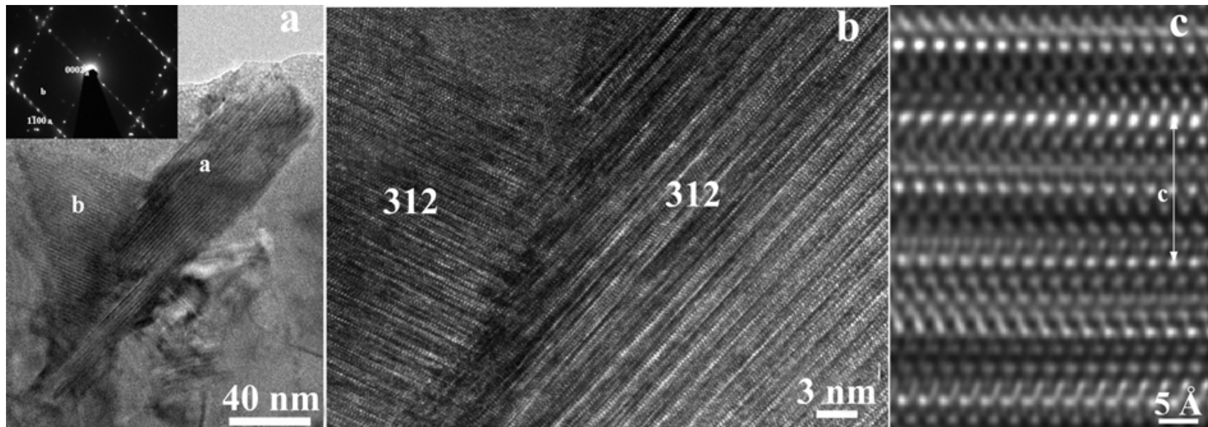

Fig.4. (a) Cross-sectional transmission electron microscopy image, (b) lattice image, and (c) corresponding selected diffraction area electron diffraction pattern from the sample deposited at 650 °C.

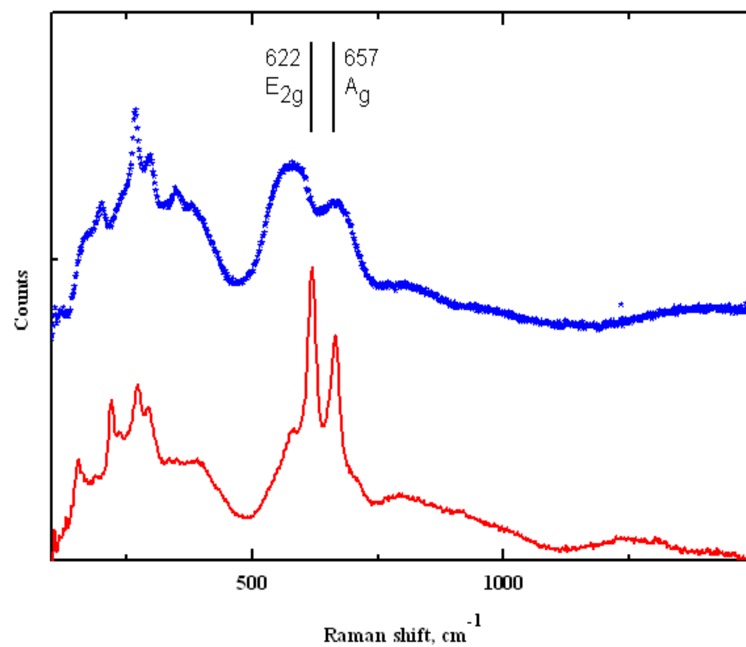

Fig5. Raman spectra from samples deposited at 610 ^{0}C (top spectra) and 650 ^{0}C.

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