SYNTHESIS AND ELECTRICAL PROPERTIES OF NANOCRYSTALLINE TITANIUM CARBIDE THIN FILMS

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Abstract

The main objective of this research work was to synthesize and to characterize structural and electrical properties of nanocrystalline titanium carbide thin films. The spin coating method was used to synthesis titanium carbide thin films, which were obtained from the HCl etching of MAX phase Ti_3AlC_2, The structural and morphological properties of the obtained films were characterized with XRD and SEM. EDXRF confirmed that aluminium (Al) was removed by etching, and the disappearance of Ti_3AlC_2 peaks were revealed from XRD profiles. From the SEM images it was revealed that the fabricated nanocrystalline films composed of several flakes and their sizes up to a few hundred nanometers. The typical microstructure of nanocrystalline titanium carbide thin films consisted of plate like grain and the grain size could be controlled by varying sintering temperature and time. Resistivity measurements were also performed with a four point probe method. The obtained results showed that nanocrystalline titanium carbide thin films could be used for transparent conductive electrodes.

Keywords: MAX Phase, Ti_3AlC_2, HCl, XRD, SEM, Resistivity

Introduction

Two-dimensional (2D) materials, such as graphene, are well known to have unique properties and important applications. In general, 2D materials are produced by exfoliating layered 3D materials with weak Van Der Waals-like coupling between layers. During the last decade, some 2D materials such as hexagonal boron nitride, metal oxides, and chalcogenides have been synthesized by chemical exfoliation or mechanical cleavage of layered 3D precursors. However, there was no report on the synthesis of 2D nanocrystalline materials by exfoliation of layered solids with strong primary bonds until [Naguib et al.] the synthesis of two-dimensional transition metal carbides by HF exfoliating from MAX phases: Ti_3AlC_2, Ti_2AlC, etc.

MAX phases materials are a confirmed class of ternary transition metal carbides or nitrides with a $M_{n+1}AX_n$, chemical formula: M is transition metal, A represents mostly elements from the III A or IV A groups such as Al, Ga, Si, or Ge, X is C and/or N and n = 1, 2, or 3. The etching process removes the A-atoms layer connecting single MX stacks and produces an exfoliated structure where multiple lamellas are piled close to each other but partially separated in an accordion-like structure. The most fascinating feature shown by MXenes is likely their ability to replace A atoms with surface terminating functional groups (typically -OH, -O and -F) which adsorbs on the layers and interact forming weak bonds. Therefore, MXenes have a formula of $M_{n+1}X_nT_x$, where T stands for a generic surface termination group. Thanks to this peculiarity, mechanical action can laminate the exfoliated structure and generate single- or few-layered flakes which can be easily dispersed both in aqueous and non-aqueous suspensions. MXenes possess a unique combination of high electrical conductivities and hydrophilicity. They are thus being

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explored for a host of applications, such as electrodes for energy storage, transparent conductive coatings, water purification, and electromagnetic interference shielding, among others.

Experimental Procedure

The MAX phase synthesized in this research work was Ti_3AlC_2. The Ti_3AlC_2 powder was synthesized by mixing of titanium powder (99.5%, China), Al powder and graphite in a 3:1:2 weight ratio and dry ball milling at 500 rpm for 12 hours. The mixed powder was cold pressed to obtain compacted pellet to avoid the presence of air embedded in the mixed powder. The obtained pellets were sintered in homemade tube furnace under the flow of nitrogen at 1000°C for 2 h, at a heating rate of 10 °C/min. The MAX phases powder produced were cooled to room temperature, and the resulting powder compacts were ball milled again to obtain powder. The MAX phase Ti_3AlC_2 powders were sieved through meshes to obtain uniform particles of size less than 10 μm. The 1 g of sieved precursor powders were immersed in 20 ml of HCl acid in a plastic container and stirred at 500 rpm for different etching time. After etching with HCl, the residues were filtered and washed several times using de-ionized (DI) water and centrifuged at 3500 RPM for a few minutes and the liquid was decanted and fresh DI water was added to disperse the sediment. This step was repeated until the decanting liquid had a pH of approximately 5. The obtained Ti_3C_2 powders were dry in vacuum oven at 200 °C for 1 h. The dry powder were mixed with ethanol and deposited onto the chemically cleaned Si substrate using spin coating method. The structural and morphological properties of the obtained films were characterized with XRD and SEM. EDXRF was used to confirm the removing of Al by HCl etching. Electrical resistivities were also analyzed with four points probe method.

Results and Discussion

XRD analysis

X-ray diffraction (XRD) was conducted on RIGAKU multiflex X-ray diffractometer in 10°-70° 2θ range. The XRD pattern of MAX phase Ti_3AlC_2 powders as starting materials was shown in Fig. 1.1. The pattern show peaks corresponding to quite pure Ti_3AlC_2. They could be indexed as hexagonal structure (JCPDS No.52-0875). Fig. 1.2 shows the XRD patterns of samples exfoliated by concentrated HCl at room temperature for 12 h, 24 h and 36 h, respectively. Both 12 h and 24 h etched samples still remain in MAX phase Ti_3AlC_2. In the XRD pattern of 36 h etched sample, the strongest peak of Ti_3AlC_2,(1 0 4) peak at 40°, obviously decreases. It was revealed that the some portions of Ti_3AlC_2 were etched with HCl to form Ti_3C_2. And also (0 0 2) peak at 10° and (0 0 4) peak at 20° were divided into two minor peaks. One minor peak was found in its original position, which belongs to Ti_3AlC_2. The other minor peak moved to low 2θ angle, which belongs to newly formed Ti_3C_2. It could be noted that at least 36 h was required to exfoliate Ti_3C_2 with HCl.

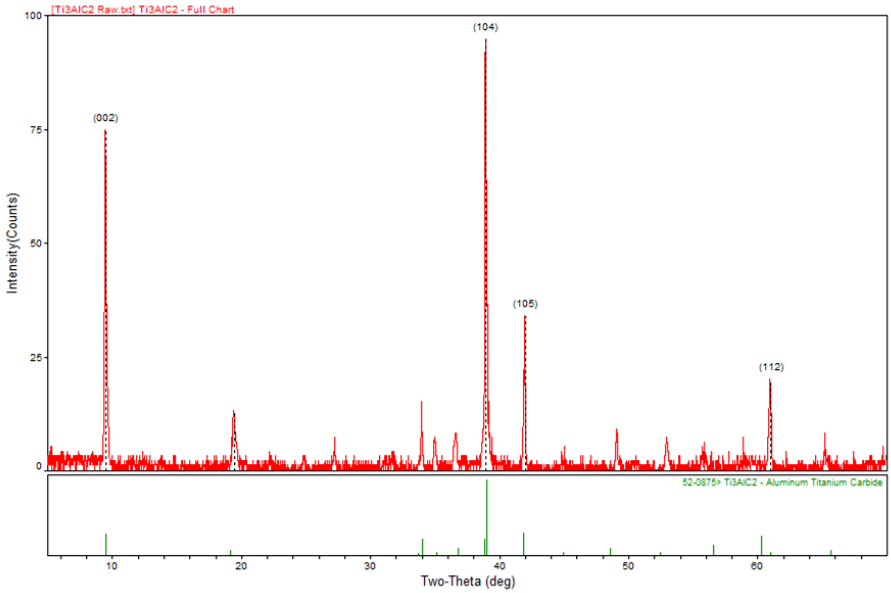

Figure 1 XRD profile of obtained MAX phase Ti_3AlC_2 powder.

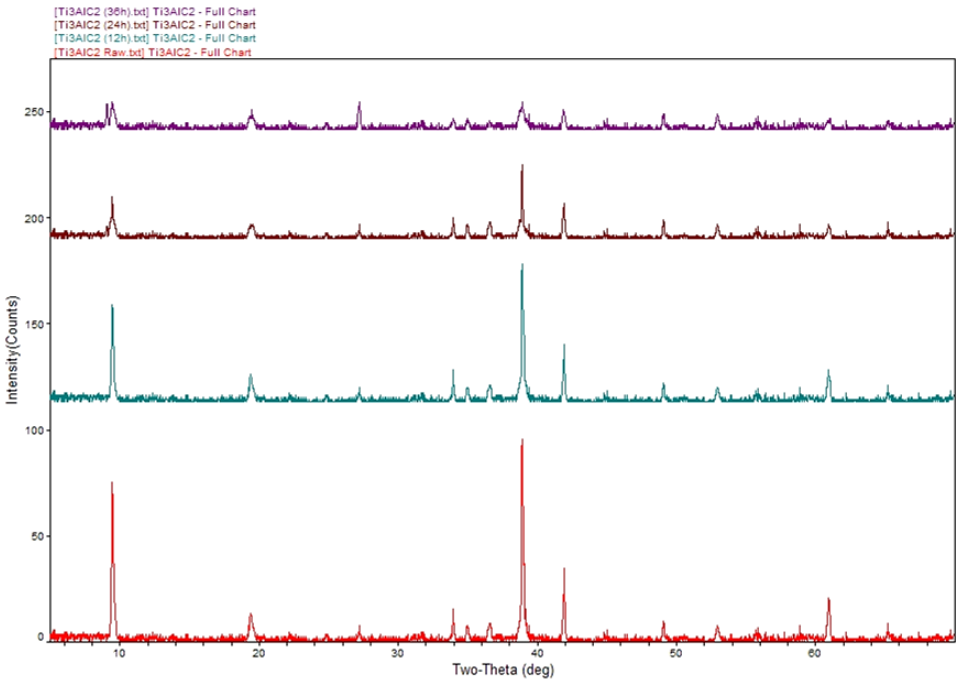

Figure 2 XRD patterns for HCl exfoliated powder for 12 h, 24 h and 36 h.

SEM analysis

The surface morphological properties of the obtained Ti_3AlC_2 powders were characterized through SEM microscopy. The SEM micrograph of obtained Ti_3AlC_2 powders was shown in Fig. 3. It was revealed that the average particle dimensions were smaller than sieve mesh and the agglomerates found in the 5 μm to 10 μm range. And MAX phase particles showed closed packed structures, where adjacent layers stack on each other by A-atoms.

Fig. 4(a),(b) and (c) showed the SEM images of exfoliated Ti_3C_2 particles for different etching time. As shown in Fig. 4(a) and (b), only partial exfoliation appeared in Ti_3AlC_2 grains after 12 h or 24 h etching. When the etching time was extended up to 36 h, more exfoliation was achieved and as shown in Fig. 4(c). The whole grain exfoliated into thin layers with uniform thickness was clearly visible. The average thickness of etched Ti_3C_2 layer was observed to be 60 ± 5 nm, which corresponds to roughly 30 Ti_3C_2 layers. Surface morphological natures of spin coated nanocrystalline Ti_3C_2 thin film was shown in Fig. 5.

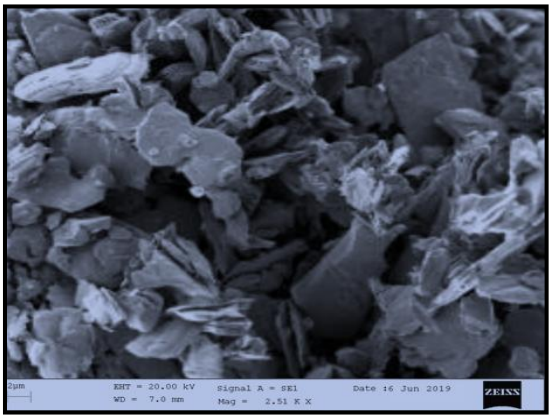

Figure 3 The SEM micrograph of obtained MAX phase Ti_3AlC_2 powders.

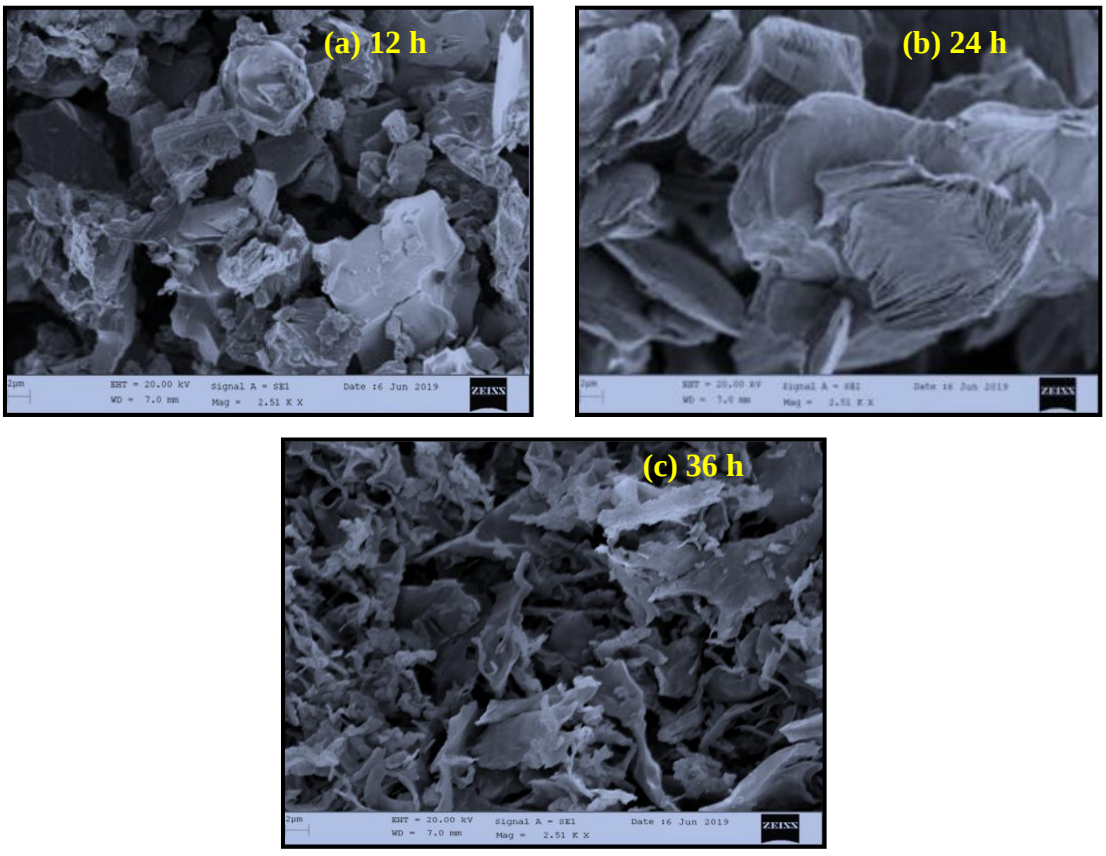

Figure 4 SEM images of exfoliated Ti_3C_2 for different etching time(a) 12 h (b) 24h and (c) 36 h.

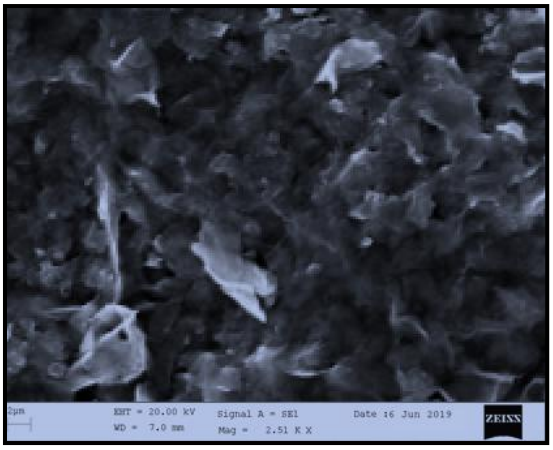

Figure 5 SEM image of spin coated Ti_3C_2 thin film on Si Substrate.

EDXRF analysis was used to confirm the formation of Ti_3C_2. From elemental analysis which showed that the Al content had reduced by HCl etching. The atomic content ratio of Ti: Al: C: O: Cl was observed to be 81% : 0.98% : 16.6% : 1.2% and 0.2%, respectively.

Electrical Properties

The four points probe technique was used for measuring the electrical resistivity of fabricated thin films and it was observed that the resistivities of obtained thin films vary with amount of Al content in the Ti_3C_2 precursors. The electrical resistivities of Ti_3C_2 thin films obtained from MAX phase Ti_3AlC_2 for different etching time were compared. The electrical resistivity of Ti_3C_2 from 12 h etching was observed to be 776 ± 10 μΩcm and that of the electrical resistivities of Ti_3C_2 from 24 h and 36 h etching were also observed to be 432 ± 10 μΩcm and 156 ± 10 μΩcm. Therefore, the Ti_3C_2 films obtained from 36 h etching was more conductive than the other samples from shorter etching time. The electrical resistivities obtained for Ti_3C_2 films in this work compared to the best values reported in literature for this material were tabulated in Table 1.1.

Table 1.1 The electrical resistivities obtained for Ti_3C_2 films in this work compared to the best values reported in literature for this material.

Ti_3C_2 Sample Type	**Electrical Resistivity (μΩ·cm)**	**Reference**
Ti_3C_2 from 12 h etching	776± 10	This research work
Ti_3C_2 from 24 h etching	432± 10	This research work
Ti_3C_2 from 36 h etching	156± 10	This research work
Spin-coated film	154 ± 7	Dillon AD, Ghidiu MJ, et al.
Epitaxial thin film	176 ± 2	Halim J, Lukatskaya M, et al.
Single $Ti_3C_2T_x$ flake	204 ± 44	Lipatov A, Alhabeb M, Boson A, Gogotsi Y. et al
Electrosprayed film	340	Ali A, Belaidi A, Ali S, Helal M.et al
Vacuum Filtered	220 ± 10	Li C, Kota S, Hu C, Barsoum M. et al

Conclusion

Nanocrystalline Ti_3C_2 thin films with hexagonal structure were successfully prepared. The influences of temperature, time and the source of Ti_3AlC_2 on the exfoliating process were studied and researched. Powder compacts partially containing Ti, Al and C were used to synthesize MAX phase Ti_3AlC_2 powder. The best condition to synthesize Ti_3C_2 was achieved in this work, which was etching for at least 36 h at room temperature in HCl. The nanocrystalline Ti_3C_2 powders were readily separated from other phase present, such as Al_2O_3 and TiC, by simply washing and filtrating. The structural and morphological properties of the obtained films were characterized with XRD and SEM. EDXRF confirmed that aluminium (Al) was removed by etching, and the disappearance of Ti_3AlC_2 peaks were revealed from XRD profiles. From the SEM images it was revealed that the fabricated nanocrystalline films composed of several flakes and their sizes up to a few hundred nanometers. The typical microstructure of nanocrystalline titanium carbide thin films consisted of plate like grain and the grain size could be controlled by varying sintering temperature and time. Electrical resistivities measurement was conducted with four probes resistance measurement method. It was revealed that Ti_3C_2 films obtained from 36 h etching was more conductive than the other samples from shorter etching time. Its high conductivity properties could be applied in the transparent conductive oxide applications and DSSC solar cells applications.

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