Research Article

Synthesis of nanocrystalline titanium nitride by microwave plasma technique

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Abstract
Nano-crystalline titanium nitride was prepared by the microwave plasma synthesis technique by optimizing microwave process parameters such as power, gas flow rate and pressure based on the stable plasma. Synthesized nanocrystalline titanium nitride was characterized to determine the structural properties such as nanocrystallinity, particle size, morphology, surface area and chemical elemental analysis using X-ray diffraction, transmission electron microscopy, scanning electron microscopy, micromeritics ASAP 2020 and X-ray photoelectron spectroscopy respectively. The results showed that synthesized titanium nitride nano-powders were crystalline, spherical in shape, the size in the range of 20–100 nm, the surface area of the nanocrystalline to be 49 m^2/g and good functional properties with 90–98% purity.

Keywords Nano-crystalline titanium nitride · Microwave · Surface morphology · X-ray photoelectron spectroscopy

1 Introduction

Nanotechnology has been regarded as an emerging technology in various industrial fields such as, magnetism [1], electronics [2], solar cell [3], biosensors [4], drug delivery [5], etc. Titanium nitride (TiN) nanopowder finds many applications such as wear resistance coatings, medical implantation, gate electrode in metal oxide semiconductor circuits and many more due to greater hardness, conductivity and chemical stability. The application of nanotechnology mostly focuses on chemical properties, but less work has been reported on mechanical structural applications.

Many researchers [6–10] have worked extensively on synthesizing different types of nanopowders to fulfill the requirement of present day applications. Vasilieva et al. [6] worked on synthesis of metal-based nanopowders using aerosol synthesis method. The powders synthesized exhibit single domain magnetism, hence, they find applications in magnetic tapes [7], ferrofluid [8], magnetic refrigerants [9] etc. Chau [10] synthesized Ni nanopowder using microwave plasma (MWP) method in the particle size range of 35–57 nm which finds application in the area of medical diagnosis and catalysis. Chau et al. [11] synthesized pure silver nanopowder using MWP achieving the production rate of 0.70 g/min which finds potential application area of catalysis and conductive coating. Vaidhyanathan et al. [12] worked extensively on the synthesis of TiN nanoparticles using MWP method. TiN is used as a diffraction barrier in large scale integration device for interconnect metallization [13]. Aluminium nitride is used as an electronic substrate because of its excellent thermal compatibility and non-reactivity with silicon. Vanadium nitride is used in the industry as a catalyst because of its selectivity and stability [14]. Gallium nitride (GaN) is one of the most promising wide band gap (3.38 eV) materials for short wavelength optoelectronic devices and has potential application in high-temperature electronics industry. In other hand, many researchers [15–18] have been found to enhance the physical and functional properties of ceramic nano powder by reducing residual stresses using annealing and heat treatment. Only a few researchers have worked extensively on syntheses of TiN crystalline nanopowder using microwave plasma technique. The objective

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of the work was to develop high quality nano-crystalline TiN powder using standardized microwave prameters and characterize them for structural analysis. Microwave technology enables extremely fast synthesis of Titanium nitrate nanoparticles with better quality compared to other techniques.

2 Experimental study

Initially, numbers of trials were conducted for stable plasma with various microwave operation parameters, such as, microwave power (1.45 kW), gas flow rate (10–40 l/min) and pressure (1–4 kg/cm^2). The plasma sustained for more than 30 min is considered as stable plasma and that condition was used for synthesis of TiN nanocrystaline powders. The optimized process parameters are microwave 1.45 kW, gas flow rate 20 l/min and pressure 2 kg/cm^2 for 30 min steady state plasma. The liquid precursor's titanium tetrachloride ($TiCl_4$) is used as a raw material for TiN nanocrystaline powder synthesis. The microwave was generated in the nitrogen environment (1 bar pressure) in a cylindrical quartz tube. Nitrogen and hydrogen gases were used as plasma forming and carrier gases to feed the gaseous stream precursor into tail nitrogen plasma flame. The mixture of 96% of argon and 4% oxygen by volume was used as a reactive gas for synthesis of TiN nanopowder. The liquid-precursors are vaporized in the evaporator and mechanical controlled constant rate precursors vaporous into the nitrogen plasma chamber.

The possible TiN formation mechanism is complex as it is reduced at higher reactant partial pressures. The overall reactions are

1. Complex forming a reaction path of the gas phase
   $TiCl_4 + 2NH_3 \Leftrightarrow TiCl_4{-}NH_3$ (yellow solid)
2. TiN nanoparticle formation reaction path
   $x(TiCl_4{-}2NH_3) + (8{-}2x)NH_3 + (6 - x)TiCl_4 \Leftrightarrow 6TiN + N_2 + 24\,HCl\ (1 < x < 4)$
3. TiN formation reaction path
   $6TlCl_4 + 8NH_3 \Leftrightarrow 6TiN + N_2 + 24HC1$

The output product is determined by the above three reaction paths. In order to avoid the complex forming gas phase reactions, the experiments are to be carried out in microwave reactor.

The synthesized TiN nanopowders were quenched in the water cooling reaction chamber and finally collected in the drum fitted with filter bag. TiN is formed in the temperature range between 1100 and 1600 °C at 1 bar nitrogen pressure with release of energy of (− 336 kJ/mol).

The phase transformation and crystallization behavior of synthesiszed TiN crystalline powder was investigated by X-ray diffraction (XRD) technique. The TiN sample was studied and recorded on a Phillips X'pert diffractometer with Cu-Kα radiations in a 2θ range of 5°–90°. The TiN nanocrystalline powders, surface morphology were studied using high resolution SEM (HR-SEM), Hitachi S-4300 instrument. A thin layer of the powder was spread onto a double-side carbon tape and then coated with gold using a sputtering system to ensure the electrical conductivity of the powder. Tin powder was examined for crystal (particle) size and shape of the nanopowders using the FEI Technai G20.

The surface area of the TiN compound was determined using Micromeritics' ASAP 2020 BET. The samples were degassed by by heating at 350 °C for 2–3 h to remove the unwanted vapors and gases absorbed at the sample surface. A known amount of nanopowder sample was taken in the sample holder before filling the liquid nitrogen and then the sample was further subjected to analysis.

The surface chemistry and oxidation states of TiN nanopowders was analyzed using X-ray photoelectron spectroscopy (XPS) Omicron ESCA + instrument equipped with aluminum anodes using Al Kα radiation by irradiating with soft X-ray photons (1–2 keV) under chamber pressure of 10^{-9} mbar and sample evaporation pressure of 5×10^{-6} mbar.

3 Results and discussion

3.1 Structural analysis

The XRD pattern of the synthesized TiN nanocrystalline powder indicating shows the reflection plane are presented in Fig. 1. The planes (111), (200), (220), (311), and (222) in the XRD pattern shows the existence of cubic TiN structure using software JCPDS 38-1420. The results are in good agreement with the reports of Hojo et al. [19] where $TiCl_4$ and NH_3 reacted in the gaseous phase above 800 °K to form a crystalline TiN nanopowder. They also reported that lattice parameters were directly proportional to the reaction temperature and increased with the increase in temperature. As observed from Fig. 1, crystallinity and phase purity was quite evident and no residual, un-reacted or oxide phases were detected. Since, there were negligible amount of impurities present in the TiN nanopowder, the chemical composition of the nanopowder changes with respect to the stoichiometry, the lattice parameter was correlated to the amount of nitrogen present in the TiN lattice [20]. The lattice constant was a = 4.235 Å almost in good agreement with a = 4.241 Å in the JCPDS card# 38-1420 [21]. The average crystallite size was estimated, using the Scherrer's equation, from the full width at half

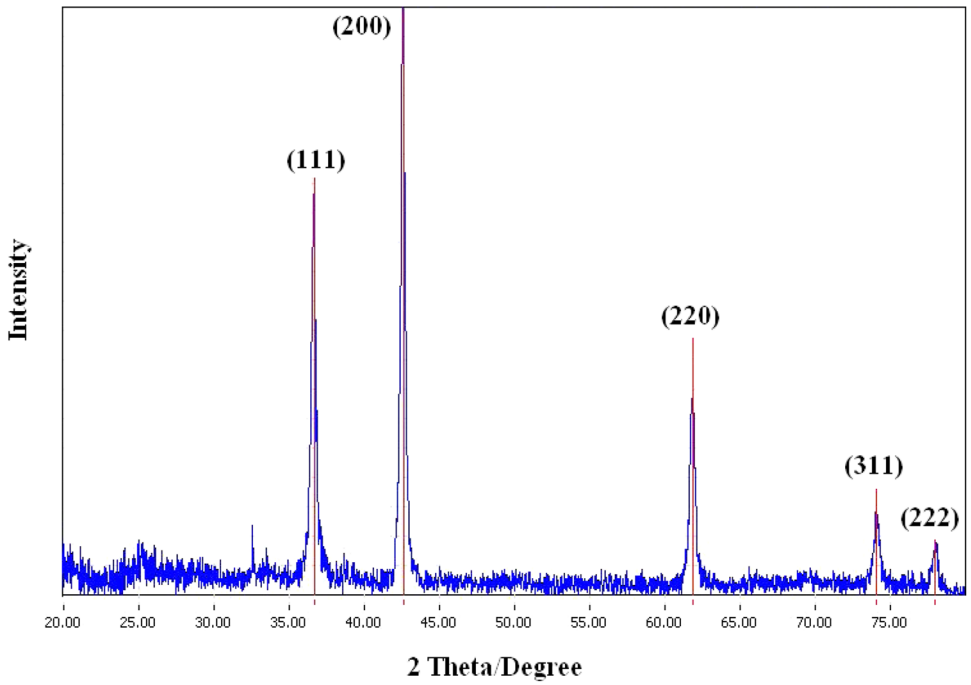

Fig. 1 XRD pattern of Si nano-powder

maximum (FWHM) of the most intense peak (200) and was found to be 18 nm.

Figure 2a, b show both the SEM and TEM micrographs of TiN nanocrystalline powder. Developed TiN particles were in the nanoscale range indicating that several particles formed soft agglomerates. The SEM micrograph showed that the particles were almost spherical and were in the range of 20–80 nm. The agglomerates found on the TEM micrographs (Fig. 2b) were due to agglomeration in the liquid film on the TEM grid during evaporation of the medium [22]. The agglomeration of the particles was also due to particle-cluster aggregation and was likely that all the agglomerates were formed on the TEM grid during the synthesis process. The particle cluster agglomerates were unlikely to form in the gas phase, because each cluster present in the gas phase will agglomerate with other clusters [23]. The average particle size as observed from TEM micrograph was in the range of 10–100 nm which is in very good agreement with the XRD analysis. It can be presumed that the particles synthesized by this method were single particle and single crystal in nature, however, there is a necessity to understand any defects or sub grain formation in the synthesized powder depending up on the application. The BET surface area of the synthesized TiN nanopowder was found to be 49 m^2/g.

The surface chemical analysis of the synthesized TiN nanoparticles was understood by the XPS analysis as shown in Fig. 3. The nanopowder surface contains Ti, N, O_2 and C. The C1*s* and O1*s* peaks indicated that there existed marginal amounts of impurity elements such as, C and O due to the adsorption of CO_2, H_2O and O_2 on the surface of

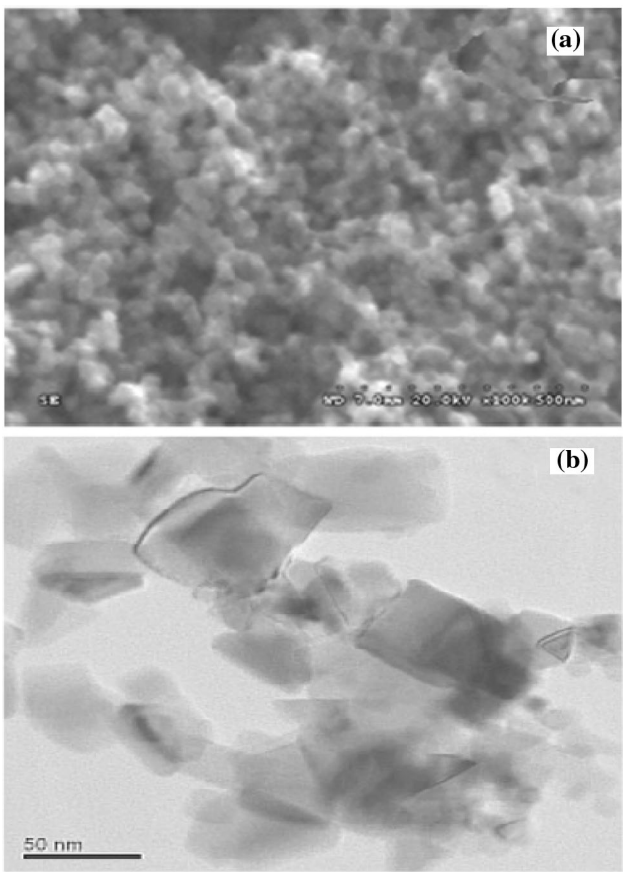

Fig. 2 Morphology of TiN nano powders, **a** SEM micrograph, **b** TEM micrographs

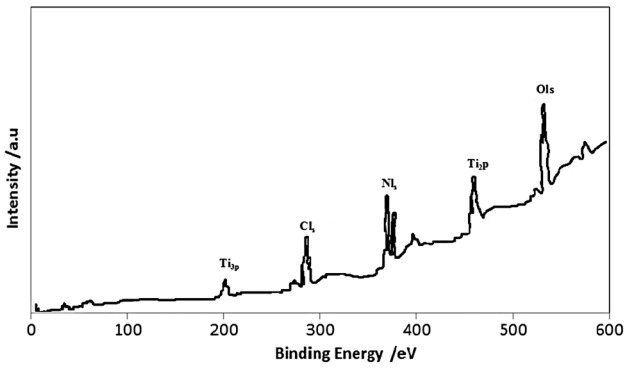

Fig. 3 XPS spectra of TiN nanopowder

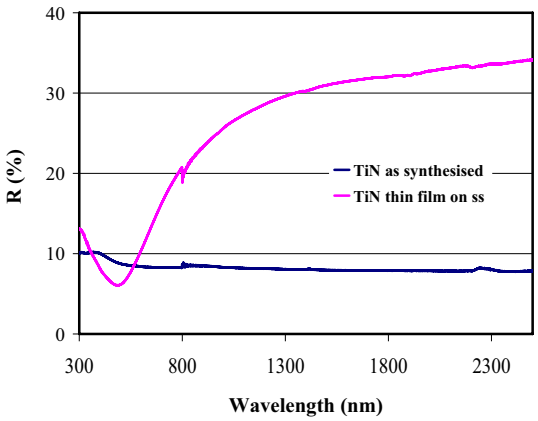

Fig. 4 Optical absorbance of synthesized TiN powder and thin film TiN

the sample or due to the surface oxidation. The N1*s* spectrum had a peak at 397.2 eV, which corresponded with the Ti 2*p*3/2 and Ti 2*p*1/2 spectra at 458.4 and 464.2 eV indicating the formation of TiN. Quantitative analysis revels the Ti:N molar ratio as 1:0.961, which closely agreed to the stoichiometric composition of TiN. These results are in good agreement with the results of Wu [21], on low temperature synthesis of nanocrystalline TiN from a single-source precursor of titanium and nitrogen.

3.2 Optical characterization of solar selective absorber coatings

The preliminary investigation of synthesized TiN for solar selective absorber coatings showed promising results. Figure 4 shows the total reflectance spectrum of as synthesized and thin film of TiN on 304 stainless steel (generally used as heat collecting elements). The thin film was made by dispersing the TiN particle in organic–inorganic binder and applied by manual spray coating. The wet film was dried at 300 °C. The resultant thin film was characterized by UV–visible absorption spectroscopy. The powder reflectance spectrum showed complete absorbance UV–visible and NIR electromagnetic spectrum and it behaved like a perfect black body with a residual reflectance of 8%. The observed spectrum was completely different from the bulk TiN, where as in the nano-range around 25 nm as observed from SEM, it behaved like perfect black body. By designing suitable coating thickness of the TiN synthesized by MWP for solar selectivity, one can realize the successful selective absorber coating for solar thermal power plant.

It can be realized from the reflectance spectra of TiN thin film on stainless steel as shown in Fig. 4. The thin film reflectance showed an average of 90% absorbent in the range of 300–900 nm. By controlling the TiN thickness, the spectral selective range can be modified from 300 to 2000 nm depending upon the operating temperature. The main requirement of the solar selective coating such as, high absorption up to 1500 nm and high reflectance above 1500 nm can be achieved. However, there is a need of separate process optimization study with respect to coating thickness and the ratio of TiN and dielectric volume percentage. In this report, it was established the feasibility of the MWP synthesized TiN for solar selective absorber coating.

The properties such as, crytallinity, particle size, surface area and chemical analysis of microwave plasma synthesized titanium nitride powder almost matched with the results obtained by other method of synthesizing previous techniques as mentioned in the Table 1. As observed from the column (3), the majority of the gas phase synthesizing techniques including MWP has used titanium tetra chloride, a liquid precursor readily dissociated at STP, as the starting raw material. In reactive ball milling and low temperature chemical synthesis micron size powder and $(NH_4)_2TiF_6$ are used as starting raw materials for the synthesis of TiN powder. As seen from the column (4) the crystallite size of the particle of reactive ball milling, gas phase, MWP, chemical and aerosol synthesis were 10, 12, 18, 20 and 29 nm respectively. All TiN particles were crystalline in nature and were cubical in structure as shown in Fig. 2. The particle sizes given in column 5 in all techniques were in the range of 10–100 mm except for aerosol processes where particle size in 2–3 µm due to agglomeration of the particles. The lattice constant "a" (column 6) for all the techniques were similar and matched with the reported value for pure TiN (4.241 Å, JCPDS cards 38-1420) which was same as that of TiN standard. The chemical analysis of the sample (column 7) showed that the TiN powder synthesized by reactive ball milling and gas phase synthesis technique had very less % impurities in the powder whereas the other 3 techniques exhibited surface oxidation in the powder. Finally, column 8 showed that the reactive gas of argon and oxygen yielded TiN with black

Table 1 Comparison of physical properties of Microwave plasma synthesized TIN nanopowder (developed method) to other synthesis techniques

References	Synthesis method	Precursor used	Crystallite size	Shape (particle size)	Lattice constant "a" in A°	Chemical analysis	Remarks
Present work	Microwave plasma technique	Titanium tetrachloride ($TiCl_4$)	Cubic TiN with crystallite size 18 nm	Spherical (10–100 nm)	4.235	Presence of impurity elements like C and O on the surface of the sample due to surface oxidation	Reactive gas used was $Ar + O_2$ which made the synthesized powder Black in color
[24]	Reactive ball milling	Titanium powder 10 µm mixed with urea (3:1)	Crystallite size (10 nm)	Agglomerated (≈120 nm)	–	Very few traces of carbon (0.5%) and oxygen (4.5%) were found on the surface of TiN nanopowder	The metal nitrides with negative large enthalpy materials with ZrN and HfN are also synthesized by this technique
[21]	Low temperature chemical synthesis	Titanium and nitrogen sources $(NH_4)_2TiF_6$	Cubic TiN (20 nm)	Agglomeration (30–50 nm)	4.241	The impurity elements such as C and O due to the adsorption of CO_2, H_2O and O_2 on the surface	The raw materials are very facile and inexpensive titanium and nitrogen sources $(NH4)_2TiF_6$
[25]	Gas phase synthesis with atmospheric microwave plasma torch	Titanium tetrachloride ($TiCl_4$, Fluka)	Cubic TiN (12 nm)	Spherical 10–80 nm	4.24	Pure TiN with no traces of chlorine as hydrogen gas was purged into the plasma system	Metal nitrides are synthesized by combining gas-phase synthesis with atmosphere-pressure microwave plasma torch
[21]	Two-stage aerosol assisted synthesis	$TiCl_4$ (0.1 M)	Cubic TiN (29 nm)	Agglomerated, 2–3 µm	4.241	TiN particle surface passivated with atmospheric oxygen	The nanopowder prepared in the 1100–1200 °C gave TIN and the powders prepared by pyrolysis at 1000–1100 °C gave titanium oxy-nitride

color. Low entropy metal nitrides can be synthesized using mechanical milling. Low temperature chemical processes used cheaper precursor (cost) and the combination of gas phase and microwave were used for metal nitride synthesis. Two kinds of TiN and Titanium Oxy nitride nanopowders can be synthesized by varying the temperature using aerosol process. The results published by Chau et al. [11] showed that the increased flow rate of plasma forming gas reduced the particle size. Depending on the type of application various process parameters can be varied to achieve desired quality of powder as explained for synthesis of titanium dioxide nanopowder.

4 Conclusion

- Microwave plasma method of synthesis was developed which produced high crystalline TiN nanopowder using $TiCl_4$ as precursor and obtained 90–98% of purity.
- Morphology of the particles was mainly spherical in shape but small, percentage particles were platelet and irregular in shape.
- Particles were soft agglomerated by themselves and their size varied from 20 to 100 nm which was confirmed by TEM studies
- TiN surface area was measured using BET and was found to be 49 m^2/g. The chemical analysis of the TiN nanopowders showed surface oxidation during the handling of the powder.
- The reflectance spectrum of synthesized TiN nanopowder for solar selective absorber coatings was recorded. The TiN nanopowder powder reflectance spectrum showed complete observance in UV, visible and NIR electromagnetic spectrum and it behaved like a perfect black body with a residual reflectance of 8% and TiN thin film on stainless steel showed an average of 90% absorbent in the range of 300–900 mm.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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