Synthesis of Ti, Ga, and V Nitrides: Microwave-Assisted Carbothermal Reduction and Nitridation[†]

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A simple, novel, and fast method of preparation of metal nitride powders (GaN, TiN, and VN) using microwave-assisted carbothermal reduction and nitridation has been demonstrated. The procedure uses the respective oxides and amorphous carbon powder as the starting materials. Ammonia gas is found to be more effective in nitridation than high-purity N_2 gas. Complete nitridation is achieved by the use of a slight excess of amorphous carbon. Metals themselves are not found to be effectively nitrided. The products were characterized using XRD, TEM, and SAED and found to possess good crystallinity and phase purity. The method can be of general applicability for the preparation of metal nitrides.

Introduction

Metal nitrides possess very high thermal, mechanical, and chemical stabilities. Several of them are also characterized by low densities and are therefore of great technological interest. TiN is a well-known diffusion barrier for aluminum interconnect metalization in VLSI device technology.[1,2] It also finds its application in metallurgy, where it is widely used as a gold-colored hard coating on tool parts.[3] GaN is one of the most promising wide-bandgap materials (3.38 eV) for short-wavelength optoelectronic devices[4] and has potential for applications in high-temperature electronics and in realizing blue-UV lasers.[5] VN is an important catalyst known for its stability and selectivity.[6] Most of the applications are based on the use of bulk nitrides either as targets for thin-film applications or as bulk devices. The conventional procedures for the synthesis of these important nitrides in bulk form are, however, extremely tedious, involving many cumbersome steps. They often require the use of atomized metal powders, very precise temperature-programmed reaction controls,[7] laser heating at high pressures,[8] prolonged high-temperature carbothermal reduction under nitrogen atmosphere,[9] heating the respective oxides for several hours in continuous flow of ammonia,[10] etc. Recently use of microwaves has been found to offer several advantages for the synthesis of inorganic materials compared to conventional methods. The foremost of them appear to be the very short time scales involved in the preparation and the reactant selectivity during energy transfer from the microwave field.[11−13] Furthermore, the high reaction rates during microwave irradiation open the possibility of synthesizing metastable phases.[14] Recently efforts have been made to accelerate selected chemical reactions and simplify the synthetic processes using microwave irradiation.[15−21] We have now developed a novel, simple, and fast carbothermal reduction cum nitridation (CTR/N) route using microwave irradiation for the preparation of these important metal nitrides.

In most cases where microwave heating is involved, at least one of the reactants is found to couple well to microwaves and to heat up rapidly. A number of oxides (e.g., V_2O_5, WO_3, CuO, and MnO_2), a few halides (AgI and CuI), and several metal powders (e.g., Cu, Ti, Fe, and Co) are found to be good microwave susceptors and are heated up to 1000 K or more when irradiated.[22] Carbon powder (both graphitic and amorphous forms) is also known to be a good microwave susceptor[13,23] and has been used as a nonreactive heating source in reactions where other reactants are microwave inert.[24,25] In the present work carbon is used not only as a heating

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source but also as a reducing agent. Both nitrogen gas and ammonia were examined as the sources of nitrogen. We demonstrate that microwave irradiation enables preparation of metal nitrides in much shorter time durations and the products with good crystallinity and phase purity are formed.

Experimental Section

Three different reaction routes have been employed for nitride preparation: (i) Exposing high-purity metal powder (3−4 g) to microwaves under flowing N_2 atmosphere. (ii) Subjecting a mixture of analytical reagent (AR) grade oxide powders thoroughly mixed with high-purity amorphous carbon black in 2:1 weight ratio (taken in a silica crucible) to microwave irradiation under dry ultra high pure N_2 (99.999%; O_2 < 10 ppm) flow. (iii) Conducting a reaction similar to that of (ii) in NH_3 atmosphere for the same durations of time. (For example, in the case of TiN preparation, reaction (i) was carried out by exposing 3 g of high-purity (99.999%) Ti metal powder to microwave irradiation for about 35 min; reaction (ii) was carried out for 35 min using AR grade TiO_2 (99% purity) and amorphous carbon; and reaction (iii) was performed using the same ingredients as in (ii) for the same durations of time.) In the case of GaN, reaction (i) of the metal with nitrogen was not performed since it is difficult to handle liquid Ga inside the microwave oven. The other two reactions [(ii) and (iii)] were carried out using high-purity Ga_2O_3 (99.9999%). For the preparation of vanadium nitride, V_2O_5 alone was exposed to microwaves in a stream of dry NH_3 since V_2O_5 is a good microwave susceptor by itself. This was in addition to procedures (ii) and (iii). After the microwave exposure, the products were allowed to cool inside the oven in the same gaseous ambient. The kitchen microwave oven (Battliboy, Eddy; operating at 2.45 GHz with a maximum power level of 980 W) and the glass reaction chamber used to create the necessary atmosphere inside the microwave cavity are shown in Figure 1a. Figure 1b shows the intense glow of the charge observed within 4 min of microwave exposure.

The temperatures of the reaction mixtures particularly in reactions (ii) and (iii) rise very rapidly even as N_2 or NH_3 gas is passed over them and the mixtures continue to glow during the entire duration of the reaction. Flashes were seen repeatedly emanating from reaction mixtures. It was found not feasible to measure the temperatures accurately because a thermocouple cannot be inserted when the microwave is on (sparking occurs in the oven). However, to estimate approximately the lower bound of the reaction temperatures, control experiments were performed where reaction mixtures were irradiated for the same length of time in ambient air in the microwave oven and temperatures were measured at the end of 5 min by switching off the power and quickly inserting a thermocouple into the charge. These temperatures are listed in Table 1. Though the present method gives a lower estimate of the temperatures measured, the relative differences can be compared and analyzed.[26] It is also found that this method is better for measuring the bulk temperature than optical pyrometry. The actual preparation conditions employed for the microwave-assisted CTR/N reactions carried out in ammonia atmosphere are also given in Table 1. The excess carbon in the products was simply washed out with distilled water, since the carbon is present as fine particles (<1 μm) and just float on water (the density of carbon is also less compared to the density of the nitrides). In the case of TiN, the dark olive-brown crystals may be separated.

The products were characterized by X-ray diffraction (XRD, Philips X-ray diffractometer, Model PW 1050/70), transmission electron microscopy (TEM, HRTEM JEOL-200CX), selected area electron diffraction (SAED), and energy-dispersive X-ray Analysis (EDAX, Model LEICA 440 i, with a super-ultrathin window detector). Table 1 lists the calculated lattice parameters of the metal nitrides prepared in this work, and the literature values are given in parentheses.

Figure 1. (a, top) Glass reaction chamber used for the containment of necessary atmosphere inside the microwave oven and (b, bottom) the intense glow of the (TiO_2 + C) mixture observed within a few minutes of microwave exposure.

Results and Discussion

The choice of amorphous carbon powder was made by considering its superior microwave-absorbing ability compared to graphitic carbon of similar particle size. It is found that amorphous carbon powder (carbon black or Vulcan XC-72) gets heated up to relatively higher temperature (1533 K) within 2 min of microwave exposure compared to graphitic carbon (1350 K), which is consistent with earlier results.[25,27] Further in the case of graphitic carbon the temperature tends to level off after 2 min heating even at maximum power setting, while in amorphous carbon the temperature continues to rise.[25] This may be because of the differences in the modes of absorption of amorphous and graphitic forms of carbon. We have earlier suggested that the microwave susceptibility in the case of graphitic carbon may originate from the activation of weak interlayer bonds while in the case of amorphous carbon from its high dielectric loss (due to presence of a variety of defects).[26] The surface activity of amorphous carbon is high because of the presence of dangling bonds. Earlier experiments also revealed that the reducing ability of graphitic carbon is also limited in the sense that

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Table 1. Preparative Conditions for Microwave-Assisted Synthesis and the Lattice Parameters of the Prepared Nitrides

compound	time of microwave exposure in NH_3 atmosphere, (min)	temp reached after 5 min exposure, in air ambient (K)	crystal syst	lattice parameters[a] (Å)
TiN	35	1073	cubic	$a = 4.242$ (4.242)
GaN	32	948	hexagonal	$a = 3.180$ (3.186) $c = 5.176$ (5.178)
VN	30	873	cubic	$a = 4.134$ (4.139)

[a] Literature values are given in parentheses.

nonlayered oxides such as TiO_2 and Ga_2O_3 are not easily reducted by it (unlike layered oxides) under microwave irradiation.[26] Although the reducing capability of amorphous carbon has not been clearly established under similar conditions, present studies revealed that amorphous carbon is particularly effective in reducing the oxides. Reduction persumably is the first step in these reactions and is followed by nitridation. We did not perform any separate experiments with graphitic carbon in view of our earlier experience. However we could observe sufficient differences in the microwave-assisted nitridation in NH_3 and molecular N_2 ambients, which we discuss below separately.

(a) CTR/N Reactions under NH_3 Atmosphere. Under microwave irradiation in NH_3 atmosphere, the carbothermal reduction and complete nitridation occurs within 35 min, which is only a fraction of the time required in conventional methods of preparation. During microwave exposure, periodic flashes of intense glow was observed, indicating the exothermicity of the reactions. Though the material turns red hot in all the cases upon microwave irradiation, the intensity of the glow was found to be less in the case of VN synthesis compared to that of TiN. This may be due to the fact that TiO_2 couples with microwaves better at high temperatures than V_2O_5. Also the reaction enthalpy in the case of TiN (−305.4 kJ/mol) is more than that in VN (−171.5 kJ/mol, assuming nitridation reactions to involve only elements). Indeed even in the experiments conducted at ambient conditions, a similar trend was observed; i.e., the temperature reached in the case of (TiO_2 + C) mixture was found to be higher than that of the (V_2O_5 + C) mixture for the same exposure durations (see Table 1). There was no evidence of melting of the reactants. Also no intermittent grinding was found necessary for the completion of the nitridation reaction. This is in contrast to the nitridation reactions involving metal powders, wherein it was observed that repeated grinding is essential for complete nitridation.[28] It was observed that though the temperature reached in the case of the (V_2O_5 + C) mixture is lower than that of the (TiO_2 + C) mixture, complete formation of VN is achieved in a relatively shorter time (see Table 1) than TiN. This we associate with the lower reduction free energy of V_2O_5 compared to TiO_2 (V^{5+} in $V_2O_5 \rightarrow V$ = 719.6 kJ/mol; Ti^{4+} in $TiO_2 \rightarrow Ti$ = 852.7 kJ/mol). When the reaction involving (TiO_2 + C) is terminated before completion (only 25 min of microwave exposure), the product was found to be a biphasic mixture of TiN (cubic) and TiO_2 (both anatase and rutile forms are seen). However, no effort was made to establish the exact times of exposure required for complete nitridation.

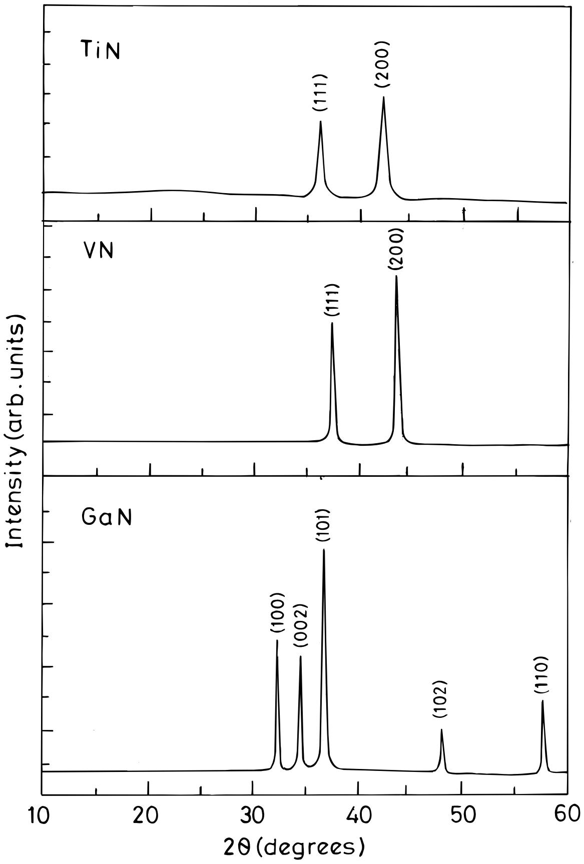

Figure 2. X-ray diffractograms of the microwave prepared metal nitrides (the background noise in the diffractograms is smoothened).

Figure 2 gives the X-ray diffractograms of the metal nitrides prepared by microwave-assisted CTR/N reaction in NH_3 atmosphere. The good crystallinity and phase purity are evident. The calculated lattice parameters agree well with the reported data.[29−31] The transmission electron micrograph and the selected area diffraction (SAED) pattern of the microwave prepared TiN are shown in Figure 3a,b. The SAED patterns taken on different particles confirmed the monophasic nature of the product. There was no evidence for the formation of corresponding carbides. To further confirm the completion of nitridation process, EDAX was performed on several samples and a typical EDAX pattern is shown in Figure 4. There is very little oxygen as indicated by the weak high energy shoulder of the main nitrogen peak. The L-edge of Ti is also convoluted into this shoulder region. The quantity of elemental oxygen present is estimated to be approximately 2% or less in these powder samples. We feel that this quantity of oxygen originates from the surfacial reoxidation and that the bulk is only pure nitride. Presence of trace amounts of carbon indicated in the EDAX spectra is

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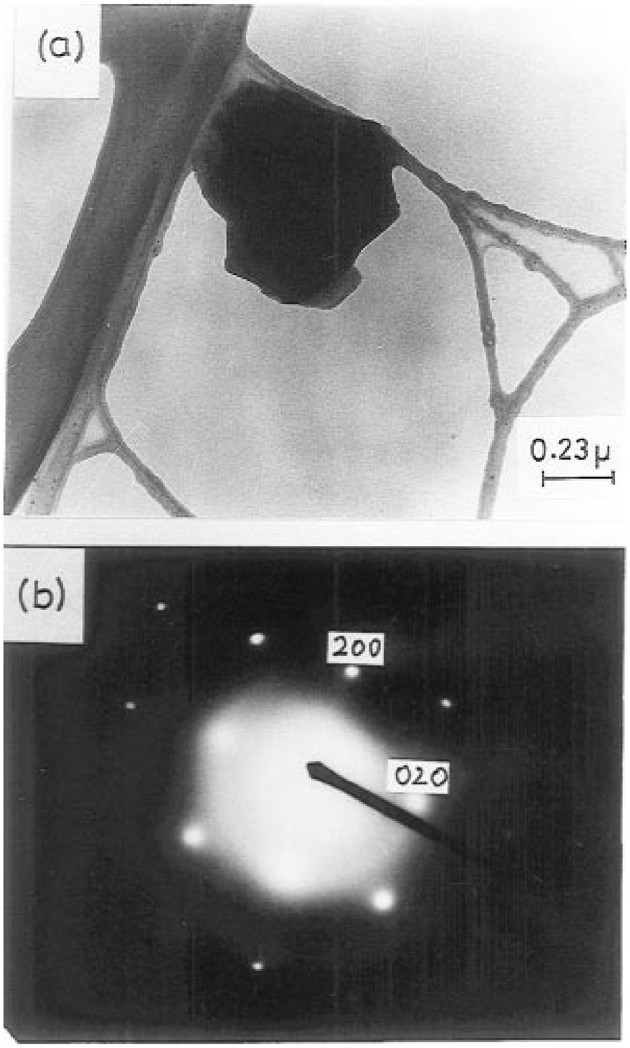

Figure 3. (a, top) Transmission electron micrograph and (b, bottom) SAED pattern of the microwave-prepared TiN.

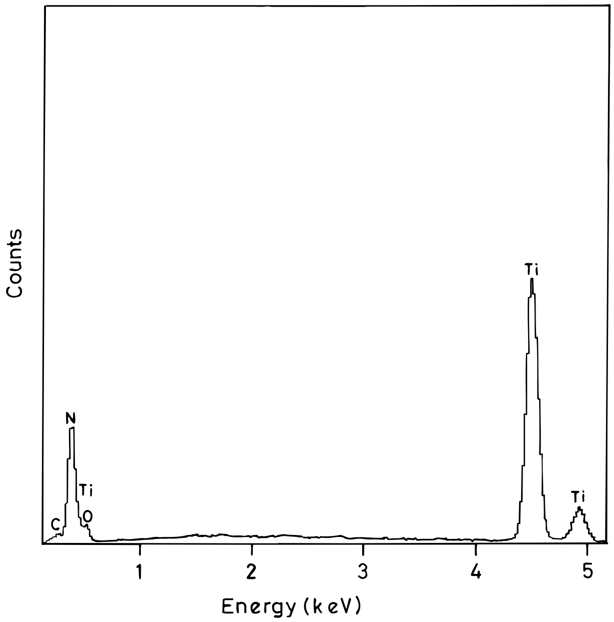

Figure 4. EDAX spectrum of TiN prepared by microwave-assisted CTR/N reaction.

attributed to the possible retention of carbon from the initial charge and not to any carbide formation.

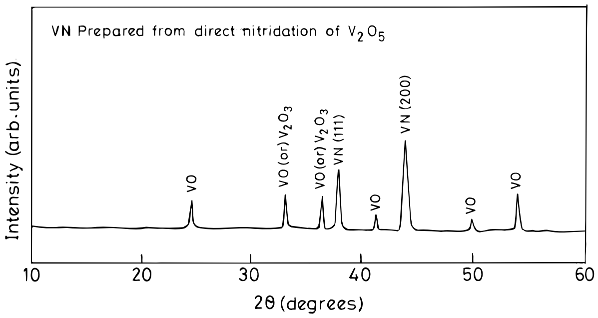

Figure 5. XRD pattern of the product obtained by the direct nitridation of V_2O_5 in ammonia atmosphere.

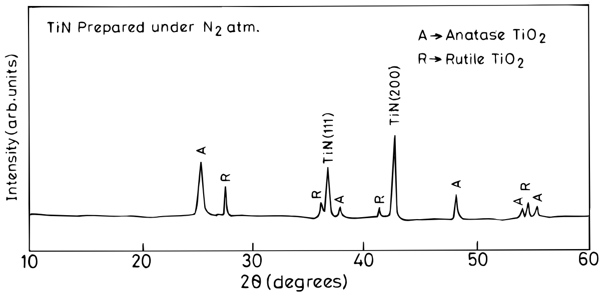

Figure 6. X-ray diffractogram of the product prepared in N_2 atmosphere, indicating clearly the incomplete nitridation.

Since V_2O_5 is itself a good microwave absorber at room temperature and NH_3 is otherwise a powerful reducing agent, V_2O_5 was subjected to microwave irradiation in flowing NH_3 atmosphere without the addition of amorphous carbon. Though nitride formation occurred very rapidly, the product was found to have some amount of lower valent vanadium oxide—secondary phase (≈30%)—even after 40 min of microwave exposure (Figure 5). This indicates that although independently NH_3 can serve both as a reducing and nitriding agent, the pathway of reduction with NH_3 leads to lower-valent vanadium oxides whose further reduction is rather sluggish. Carbon on the other hand is likely to involve a more severe reduction step which therefore obviates the above reaction limiting complication.

(b) CTR/N Reactions under N_2 Atmosphere. When a (TiO_2 + C) mixture was exposed to microwaves in ultrahigh-pure dry N_2 atmosphere for the same time durations (35 min), only 70% nitride conversion was observed and the other phase was identified as TiO_2 (Figure 6). Also it was found for any given time there was greater extent of nitridation occurring in NH_3 atmosphere than in N_2 atmosphere under identical conditions of microwave exposure. Similar behavior was observed with (V_2O_5 + C) (in this case secondary phases of lower valent oxides of vanadium were formed) and (Ga_2O_3 + C) mixtures also for the same microwave exposure conditions.

(c) Reaction of Metal with N_2. A consideration of the reaction of metal with N_2 is also important. Titanium metal powder was found to absorb microwaves efficiently when subjected to irradiation under N_2 atmosphere. The microwave absorption of Ti may be due to the eddy currents generated in small Ti particles. Occasional flashes of glow were observed at the material surface, and no melting was noticed. But the resultant product even after 30 min of exposure was found to have only metallic Ti as the major phase (more than 95%). This may be due to the fact that the temperature reached in the case of simple Ti powder is not sufficient for the formation of TiN. It will be interesting to note here that (from independent experiments[25]) the temperature reached in the microwave assisted reaction of (Ti + Si) mixture is not sufficient enough to induce the formation of titanium silicide.

(d) Mechanism of Nitridation. We now reconsider the possible reaction mechanism leading to nitridation in (a) and (b) above. Observations in reactions (a) and (b) clearly indicate that NH_3 is a better nitriding source in the microwave field compared to N_2 gas. This can be considered as an indication that NH_3 is initially transformed to NH^{2-} or NH_2^- type transient species and the nitrogen in such species more readily attach to the metal ions as a step toward nitridation. The formation of such species is likely to be a consequence of reaction of NH_3 in which it acts as a proton donor to the oxide. Oxide ions of TiO_2 abstract the protons and allows the nitrogen atom in the resulting NH^{2-} to be negatively charged so as to bind to the Ti^{4+} ion (it may be a better form of binding than the lone pair on N in NH_3 itself bonding to Ti^{4+} ions).

We therefore note that both carbon and ammonia can bring about the reduction step which precedes nitridation. But in the absence of carbon the reduction step involving ammonia is in some way self-defeating because it seems to first lead to the formation of somewhat stable intermediate valence states of the metal ion, which is not further reduced easily by NH_3 itself. The nitridation becomes very sluggish. On the other hand, CTR/N reaction using N_2 also becomes very sluggish since N_2 is not as effective as NH_3 for attachment of nitrogen to the metal ion (because the latter can produce NH_2^- and NH^{2-} as transient species). Thus we note that a combination of amorphous carbon and ammonia provides the best chemistry needed for the microwave-assisted CTR/N reactions of these oxides. The intermediate valancies of the metal ions are readily reduced by amorphous carbon at the high temperatures attained in the microwave field and the transient species such as NH_2^- and NH^{2-} lead to a more effective attachment of nitrogen to the metal ions. The formation of transient species from ammonia are only hypothesized in this paper but not yet experimentally established.

Conclusions

Technologically important metal nitrides can be prepared in powder form using microwave-assisted CTR/N reactions which are very facile, fast, and simple. Microwave irradiation not only accelerates the CTR/N reactions but also yields products of good crystallinity and structural uniformity. Amorphous carbon and NH_3 are found to provide the best combination of reducing and nitriding agents for the CTR/N reactions carried out using microwave radiation. The present method also highlights an easy way of creating the desired atmosphere (either reactive or inert) inside the microwave cavity. The suggested microwave method appears to be quite general and the comparison of the various properties of microwave-prepared nitrides with those prepared by conventional means is underway.

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