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Formation of B, Al, Ga, and Si nitrides from their oxides: a reactive laser ablation study

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Abstract

Nitrides such as Si_3N_4 and GaN are made by the reaction of the respective oxide with N_2 or NH_3. In order to understand the mechanism of formation of nitrides, reactive laser ablation of B_2O_3, Al_2O_3, Ga_2O_3, and SiO_2 in pure form, as well as in mixture with carbon, has been carried out in an atmosphere of nitrogen or ammonia in a pulsed supersonic jet. The reaction of N_2 with SiO_2 gives nitridic species such as Si_2N_y ($y \leq 5$) in the vapor phase. On reaction with N_2 in the presence of carbon, B_2O_3 and Ga_2O_3 yield species of the type B_xN_y and GaN_y, respectively. Nitridic species are preponderant in the reaction with ammonia only in the case of SiO_2. Al_2O_3 predominantly gives oxynitridic species under the reaction conditions examined.

Keywords: A. Electronic materials; A. Nitrides; A. Oxides; B. Laser annealing

1. Introduction

Nitrides of elements such as B, Al, Ga, and Si are all of considerable technological importance because of many interesting electronic, mechanical, and other properties that they possess [1,2]. In the last few years, nanowires and nanotubes of some of these nitrides have been prepared, and in all such preparations, the basic reaction is between the parent oxide and ammonia or nitrogen at relatively high temperatures ($\geq$1000 °C), sometimes carried out in the presence of carbon. Thus, boron nitride has been synthesized by the reaction of boric oxide (B_2O_3) with ammonia or nitrogen in the presence of carbon [3,4]. AlN has, similarly, been prepared using oxide precursors in the presence of ammonia [5], while GaN is produced from gallium sub-oxide (GaO_x) obtained by reacting Ga_2O_3 with ammonia [6,7]. Silicon oxynitride (Si_2N_2O) and Si_3N_4 are obtained by the reaction of SiO_2 or silicon sub-oxide

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(SiO_x) with ammonia or nitrogen [8,9]. Some of these reactions are favored by carbon. We, therefore, considered it to be of considerable importance to understand how and why the nitrides are formed starting from the oxides. The main question to be answered is the following. Are the oxynitride and nitride species formed in the vapor phase when the oxides react with N_2 or NH_3 at high temperatures? Towards this end, we have investigated the interaction of the oxides B_2O_3, Al_2O_3, Ga_2O_3, and SiO_2 with N_2 and NH_3, by carrying out laser ablation of the oxides in the appropriate atmosphere in a pulsed supersonic jet of helium. We have also examined the effect of carbon on the reaction of nitrogen with the oxides.

2. Experimental

An indigenously built apparatus [10] was used for the reactive ablation experiments. It consists of a cluster generation chamber connected to a linear time-of-flight (TOF) mass spectrometer through a gate-valve. A sample cell based on the design by Smalley and co-workers [11] was mounted in front of the pulsed supersonic valve (R.M. Jordan, USA). The reactant gas, nitrogen or ammonia, was introduced into the sample cell along with carrier gas He (99.999%) through the pulsed supersonic valve (10 Hz; width 60 μs), at a total back-pressure of ~3 atmospheres. A schematic of the reactive ablation set-up is shown in Fig. 1. The second harmonic of a pulsed Nd-YAG laser operating in Q-switch mode (6–7 ns and 10 Hz) was used for the sample vaporization. The oxide powder sample was filled in a spiral groove made in a stainless steel target rod. To perform the ablation of the oxide powder in the presence of graphite, a grooved graphite rod was machined in a similar fashion and the powder sample was painted onto it. The power of the vaporization laser was ~100 mJ/pulse. The delay of the laser with respect to the peak of the current pulse driving the pulsed valve spring was typically 90 μs. The details of the detection of the cluster species were as described elsewhere [12].

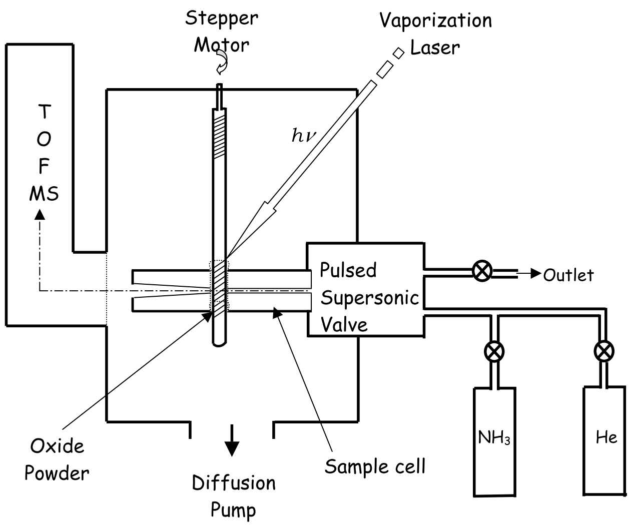

Fig. 1. A schematic of the reactive laser ablation experimental set-up.

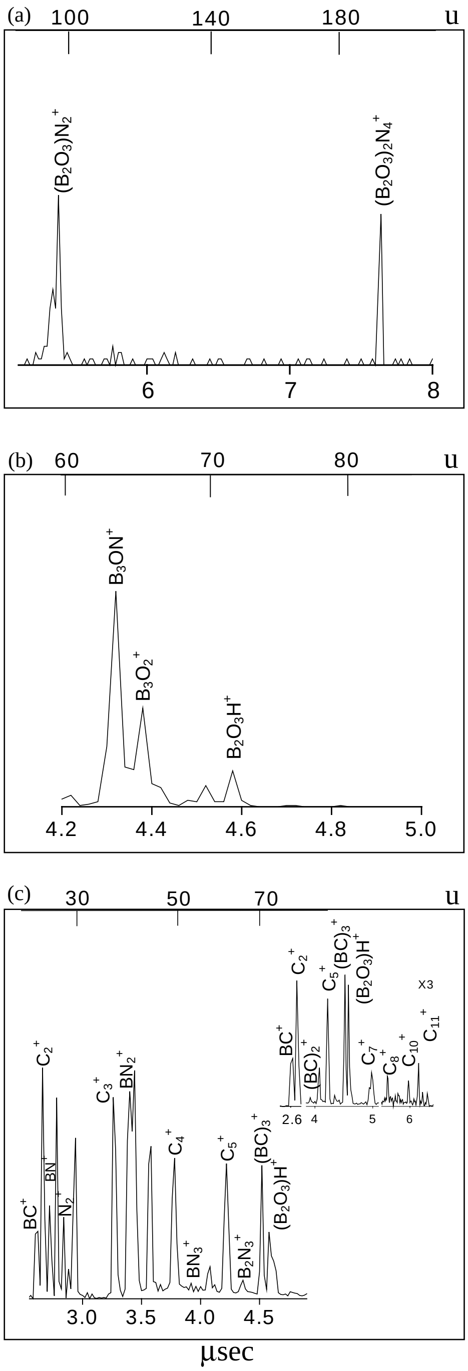

Fig. 2. Time-of-flight mass spectra of the species obtained by ablating B_2O_3 in the presence of (a) nitrogen, (b) ammonia, and (c) carbon + nitrogen. Inset shows the reaction of B_2O_3 with carbon.

3. Results and discussion

Reactive laser ablation of B_2O_3 in the presence of N_2 yields adducts of the type $(B_2O_3)N_2^+$ and $(B_2O_3)N_4^+$ as seen in the mass spectrum (Fig. 2a). The relative populations of these species are about a tenth of the parent B_2O_3 species. When the reaction was carried out in an NH_3 atmosphere, oxynitride species such as B_3ON^+ are found besides $B_3O_2^+$ and $B_2O_3H^+$ (Fig. 2b). The B_3ON^+ species is most preponderant, constituting a population of 58% with respect to the B^+ peak. Boron nitride species are formed when the reactive ablation with nitrogen is carried out in presence of carbon. The mass spectrum in Fig. 2c shows prominent peaks corresponding to BN^+ and BN_2^+ besides smaller intensity peaks due to BN_3^+ and $B_2N_3^+$. It is to be noted that BN_3 and B_2N are formed in the vapor phase by the laser ablation of boron nitride rod in an Ar/N_2 atmosphere [13]. Ablation of B_2O_3 in mixture with carbon produces species such as BC^+, $(BC)_2^+$, and $(BC)_3^+$ along with C_n^+ species (see inset of Fig. 2c), as expected [14].

Laser ablation of Ga_2O_3 in presence of N_2 leads to molecular attachment of N_2 to Ga or GaO giving rise to species such as GaO^+, GaN_2^+, and $GaON_2^+$, as shown in Fig. 3a. The intensities of

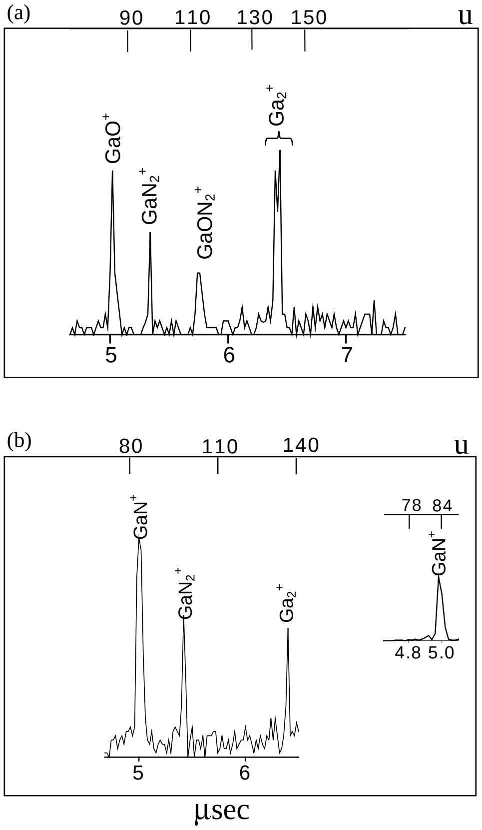

Fig. 3. Time-of-flight mass spectra of the species obtained by ablating Ga_2O_3 in the presence of (a) nitrogen and (b) carbon + nitrogen. Inset shows the reaction of Ga_2O_3 with carbon and ammonia.

these species are, however, small (about 2% with respect to Ga^+ species). In the presence of ammonia, Ga_2O_3 forms molecular adducts of the type $(Ga)_n(NH_3)_m{}^+$, with $n \leq 2$ and $m \leq 6$. When the above reaction is carried out in the presence of carbon, a prominent peak corresponding to GaN^+ is observed (Fig. 3b). The relative intensity of GaN^+ is about 17% with respect to Ga^+.

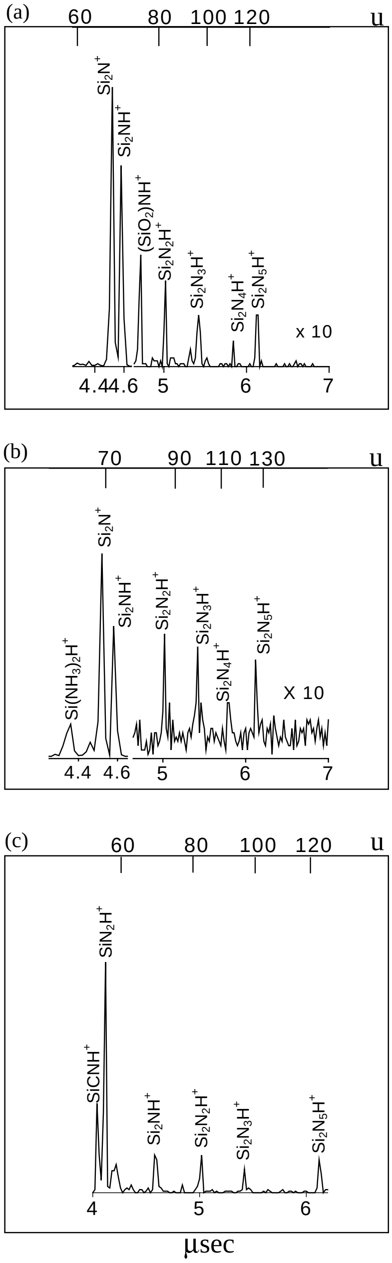

Fig. 4. Time-of-flight mass spectra of the species obtained by ablating SiO_2 in the presence of (a) nitrogen, (b) ammonia, and (c) carbon + nitrogen.

Table 1
Major types of species in the vapor phase

Metal oxide	N_2	NH_3	$C + N_2$
B_2O_3	BON	BON	BN
Ga_2O_3	GaN, GaON	$Ga(NH_3)_n$	GaN
SiO_2	SiN	SiN	SiN

A similar result was obtained when NH_3 was used instead of N_2 (see inset of Fig 3b). It may be recalled that GaN films have been reported to form by reactive ablation of liquid Ga metal in ammonia [15].

Under the conditions employed for B_2O_3 and Ga_2O_3, the reactive ablation of Al_2O_3 was also carried out. Al_2O_3 in the presence of N_2, NH_3, or $C+N_2$ produced $AlON^+$ as the dominant product along with smaller intensity peaks due to $AlON_2{}^+$ and $AlN_2{}^+$. It is known that nitridic species of Al are formed when laser ablated Al atoms are co-deposited with pure N_2 in an argon atmosphere [16].

Reactive laser ablation of SiO_2 produces nitridic species. The various nitridic species formed are Si_2N^+, Si_2NH^+, $Si_2N_2H^+$, $Si_2N_3H^+$, $Si_2N_4H^+$, and $Si_2N_5H^+$, of which Si_2N^+ and Si_2NH^+ peaks have relative intensities of about 45 and 32%, respectively, compared to $Si_2{}^+$ (Fig. 4a). The H attachment may arise from the ambient in the cluster apparatus. The Si_2N species is also known to form during pulsed laser ablation of Si rod subjected to NO_2 and N_2O [17], as well from the laser ablation of Si_3N_4 [18]. Reaction with ammonia produces a similar spectrum (Fig. 4b), with the most dominant peak corresponding to Si_2N^+. In the presence of carbon, the reactivity of SiO_2 is only marginally altered, giving rise to mass peaks due to $Si_2N_2H^+$, $Si_2N_3H^+$, and $Si_2N_5H^+$ having comparable intensities as that of Si_2NH^+ (Fig. 4c).

That the prominent species are nitrides when B_2O_3, Ga_2O_3, and SiO_2 are laser ablated in N_2, in the presence of carbon if necessary, is noteworthy. This observation suggests that the formation of nitrides is by the vapor-solid process by the mechanism as shown below:

$$MO_x(g) + \frac{y}{2}N_2(g) \rightarrow MO_xN_y(g), MN_y(g)$$

$$MO_x(g) + xC(g) + \frac{y}{2}N_2(g) \rightarrow MN_y(g) + xCO(g)$$

4. Conclusions

The present study establishes the formation of nitridic species of B, Ga, and Si on reacting the respective oxides with N_2 or NH_3. The main species formed are listed in Table 1. The study establishes that the oxides form nitride or oxynitride species in the vapor phase by interaction with nitrogen or ammonia.

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