Thermal Decomposition of NF_3 with Various Oxides

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The thermal decomposition of NF_3 by various oxides was investigated using gas chromatography, BET surface areas, and X-ray powder diffraction. The decomposition of NF_3 using alumina can occur at temperatures as low as 100 °C, with steady complete conversion for almost 4 h at 400 °C. The reaction is shown to be stoichiometric. Using Na-doped alumina, conversion of NF_3 dropped off faster than conversion with the undoped alumina. Similarly, calcium oxide did not react with the NF_3 as completely or last as long as the alumina did; even at 400 °C the conversion of NF_3 was only briefly greater than 90%. HX zeolite was also reacted with NF_3, with higher and more consistent conversion than occurred with calcium oxide and Na-doped alumina, but did not perform as well as the alumina. Over 98% conversion was maintained at 400 °C for more than 1 h. In all cases, nitrogen oxides and the corresponding metal fluorides were the only major products from the reactions. The XRD patterns confirm the presence of metal fluorides for all of the materials investigated. On the basis of these investigations, it has been concluded that of all the oxides studied, alumina is the best oxide getter for NF_3.

Introduction

In the past decade, the use of NF_3 has increased dramatically. This is primarily due to the development of NF_3 as an etching and cleaning agent in the semiconductor industry. The development of a plasma method that can enhance reaction selectivity while at the same time reduce damage and contamination has become increasingly important as the sophistication of integrated circuit technology has increased. NF_3 has managed to fill this role.

NF_3 plasmas for cleaning and etching have several advantages over the more commonly used CF_4 plasmas. NF_3 is easily stored and handled at ambient conditions. It leaves no carbonacious residue behind; the byproducts are gaseous,[1] consisting mostly of N_2, O_2, NO_x's, and the corresponding fluoride (such as SiF_4 when cleaning Si-containing materials). In addition, etch rates for NF_3 are considerably faster than those for CF_4. For example, a 20% NF_3 (balance Ar) mixture had a Si etch rate 10 times faster than pure CF_4 and 3 times faster than a 4% oxygen (balance CF_4) mixture. Selectivities for silicon over silicon dioxide have been reported as high as 50:1.[1] Also, oxygen can be mixed with NF_3 to increase the oxygenation rate of silicon,[2] or hydrogen with NF_3 to improve etching selectivity of SiO_2 with respect to Si.[3]

NF_3 has been found to be an excellent choice for cleaning many commonly used semiconductor materials such as silicon,[1,4,5] tungsten,[6] and tungsten silicide,[7] as well as other materials. It can also be used for cleaning reactor chambers[8] and reactors[9] without leaving unwanted residue behind.

Two of the biggest concerns in using NF_3 is its cost and toxicity. NF_3 costs more than CF_4 and is more toxic. The threshold limit value is 10 ppm; higher chronic doses can cause liver and kidney damage, and an acute high dosage could cause poisoning from anoxic death.[10] Two other concerns are its effect as a greenhouse gas because of a very long atmospheric lifetime and its explosive reactivity toward metal hydrides. Because of these concerns, new processes need to be developed to destroy or remove unreacted effluent NF_3.

Several types of scrubbers are currently used to trap or decompose NF_3. Incineration (with and without hydrocarbon fuels) is one of the more popular methods used. This results in NO_x and HF production. Activated carbon scrubbers are also used, but there are concerns of accidental NF_3 releases or decomposition to volatile fluorocarbons.[1,4,11] Aqueous scrubbers have never been tried because of the very slow hydrolysis of NF_3 and its low solubility in water.[12]

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Table 1. BET Surface Area Measurements of the Various Oxides before Being Reacted with NF_3

oxide	S.A. (m^2/g)
alumina	330
Na-doped alumina	233
calcium oxide	<5
HX zeolite	155

Some systems have been reported that use metals, supported metals, and oxides to thermally decompose NF_3 to nitrogen (or nitrogen oxides for oxide materials) and the corresponding fluorides. For example, consider the following patents: BN at 250−260 °C;[13,14] Si_3N_4 at ≥200 °C;[15] Cu and Ni non-oxide compounds supported on activated carbon at 100−300 °C;[16] and metal oxides and activated carbon at 200−600 °C.[17] Pure metal and metalloid systems have also been suggested, Ti was used at temperatures ≥200 °C,[18] and Si, B, W, Mo, V, Se, Te, Ge, and/or their non-oxide compounds was used to decompose NF_3 at temperatures between 200 and 800 °C.[19]

However, to choose an optimum getter for NF_3, a systematic comparison of the effectiveness of various materials is in order. In an earlier paper, we considered thermal decomposition by various metals.[20] The research presented here is concerned with the thermal decomposition of NF_3 using Al_2O_3, Na-doped Al_2O_3, CaO, and HX zeolite. Surface area measurements and X-ray diffraction were used to help explain the decomposition process, with the objective of finding the material that can consistently decompose NF_3 at the lowest possible temperature.

Experimental Section

Materials and Preparation. NF_3 (1% by mol, balance He) was purchased from Air Products and Chemicals in Allentown, PA. The following oxides were used after heating to 450 °C for 2 h in flowing He and were obtained from the following sources: γ-Al_2O_3, crushed with fines removed, from La Roche Chemicals, Baton Rouge, LA; Na doped γ-Al_2O_3, crushed with fines removed, from La Roche Chemicals, Baton Rouge LA; and CaO, reagent grade, pressed into a pellet, then crushed with fines removed, from Allied Chemical Co., Morristown, NJ. HX zeolite was prepared from NaX zeolite by ion exchange with NH_4NO_3 overnight twice, and then heated to 375 °C for 12 h. It was then pressed into a pellet, crushed with fines removed, and heated to 350 °C for 2 h in flowing He. The NaX zeolite was purchased from Alfa Products, in Danvers, MA, and the NH_4NO_3 from J.T. Bakers, Phillipsburg, NJ. Ultra high-purity grade He gas was purchased from Aero All-Gas Co., in Hartford, CT.

Reaction Process. The reactions involved successive heating of the oxide materials to four different temperatures, 100, 200, 300, and 400 °C. Approximately 0.350 g of material was placed inside a reactor made of 1/8 in. Inconel tubing plugged with glass wool. The materials were heated for 2 h at 450 °C (HX zeolite at 350 °C) in flowing He to drive off any water. Nitrogen trifluoride (1%) was passed over the oxide at a flow rate of 7.5 mL/min after the sample had equilibrated at the chosen temperature. The residence time was calculated to be about 0.2 s. Gas chromatograph analyses were done at approximately 7 min intervals. A tube furnace was used to heat the vertically placed reactor, and the thermocouple was placed in the reactor directly above the bed of oxide. See the reactor design description in a previous paper.[20]

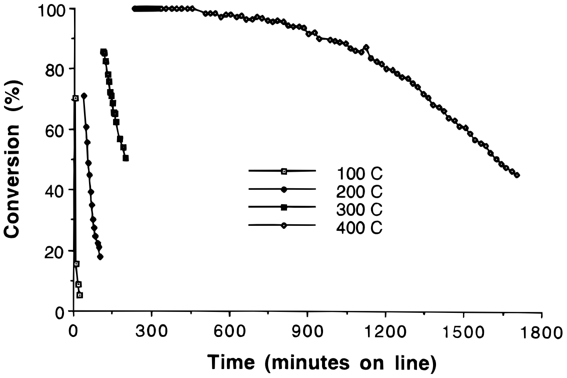

Figure 1. Conversion results for alumina.

Table 2. Summary of the Initial Conversion of NF_3 by the Various Oxides Investigated

	initial conversion (% of NF_3) (minutes conversion was maintained)			
oxide	100 °C	200 °C	300 °C	400 °C
alumina	70	71	86	100 (222 min)
Na-doped alumina	15	57	90	98 (20 min)
calcium oxide	>2	2	29	92
HX zeolite	>2	17	100 (<7 min)	>98 (91 min)

The gas chromatograph used was a Hewlett-Packard 5890 Series II gas chromatograph equipped with a thermal conductivity detector and an HP 3396 Series II integrator. A Haysep D packed column was used to separate the gases. The system can detect NF_3 to less than 0.002 mol % in the exhaust gas. The percent conversion of NF_3 was calculated based on an average of NF_3 counts obtained by bypassing the reactor.

Sample Characterization. A Scintag XDS 2000 X-ray powder diffractometer was used to identify and characterize the reacted and unreacted materials. Cu Kα radiation was used as the X-ray source, with a beam current and voltage of 45 mA and 40 kV, respectively. All patterns were compared to a JCPDS data base. Surface area measurements were done by BET, using an Omnisorp 100CX instrument with N_2 adsorption.

Results

Alumina. A 0.350 g sample of alumina, with a BET surface area of 330 m^2/g (see Table 1 for summary of BET surface areas before reaction), was heated in flowing He at 450 °C for 2 h, and then reacted with NF_3 at four different temperatures. Similar samples were heated under the same conditions, with a resulting 10% loss in mass, presumably from adsorbed water. Figure 1 shows the conversion results, and Table 2 summarizes all of the conversion results for the various oxides used. At 100 °C the conversion of NF_3 starts at 70%, but drops to 5% in 16 min. At 200 °C the conversion starts at 71% and drops to 18% in 42 min. At 300 °C conversion of 86% is reached initially, and by 87 min the conversion has dropped to 50%. Finally at 400 °C 100% conversion

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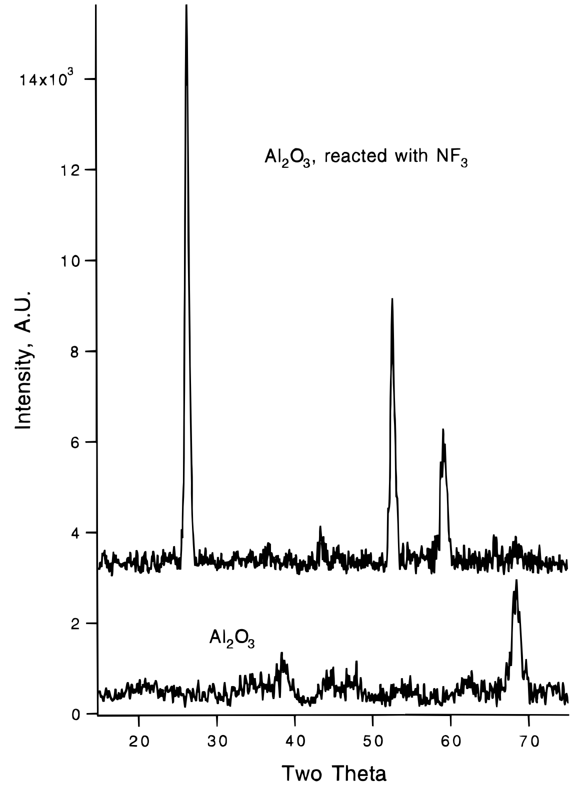

Figure 2. X-ray diffraction pattern for reacted alumina.

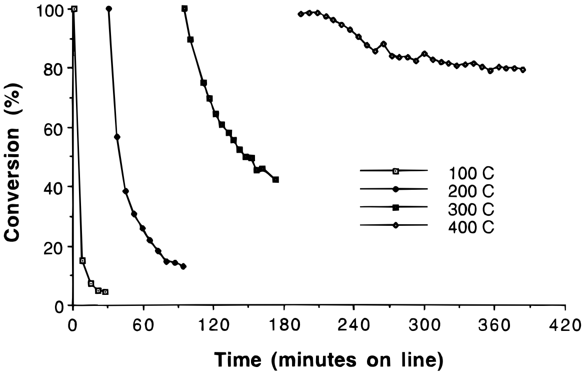

Figure 3. Conversion results for Na-doped alumina.

is reached and maintained for 222 min, and then drops to 50% at 1622 min on line, (for a total of 1392 min at 400 °C).

Major gaseous products are nitrogen oxides. After reaction the alumina sample weighed 0.460 g, for a net gain of 0.110 g. XRD results suggest that the unreacted alumina was mostly amorphous, with a broad low peak around 1.4 Å, as expected for γ-alumina. After reaction, an XRD pattern corresponding to AlF_3 was detected. Figure 2 shows these XRD patterns.

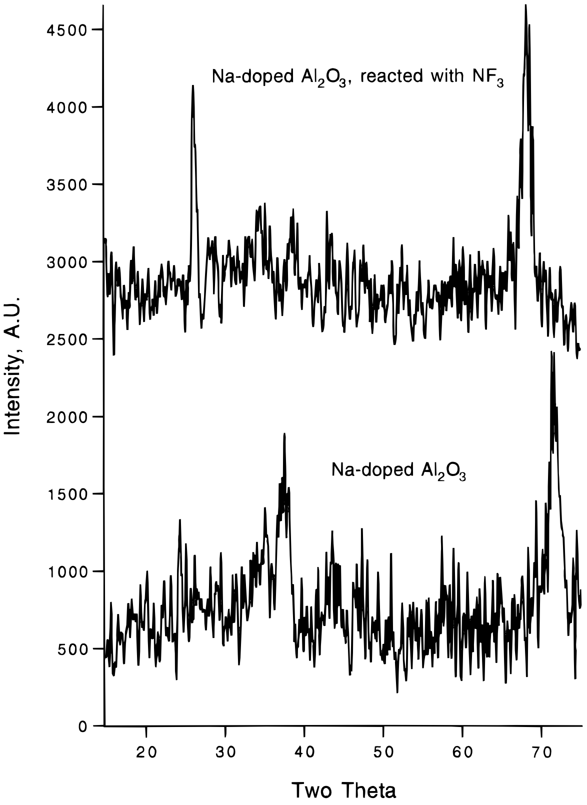

Figure 4. X-ray diffraction pattern for reacted Na-doped alumina.

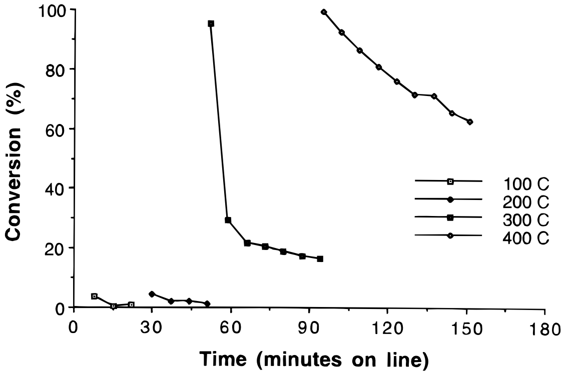

Figure 5. Conversion results for calcium oxide.

Na-Doped Alumina. A 0.359 g sample of Na-doped alumina (8% Na_2O by mass), with a BET surface area of 233 m^2/g, was reacted with NF_3 under conditions similar to those for alumina. Figure 3 shows the results of NF_3 conversion. At 100 °C the initial (highest) conversion of NF_3 is 15%, dropping to 4% within 20 min. At 200 °C, the Na-doped alumina converts NF_3 initially at 57%, and conversion drops to 13% within 56 min. NF_3 conversion starts at 90% at 300 °C, and drops to 42% 91.5 min later. Finally, at 400 °C, conversions close to 100% are obtained but maintained for only 20 min, with conversion dropping and leveling off at 80% for at least 90 min.

The XRD pattern of Na doped alumina before reaction was similar to the nondoped materials with a broad peak at 1.4 Å. After reaction, the main peak of AlF_3 can be seen, but no peaks for NaF are evident. Figure 4 shows these XRD data.

Calcium Oxide. A 0.280 g sample of CaO was also reacted with NF_3 (see Figure 5 for conversion results). The BET surface area was calculated to be less than 5 m^2/g. At 100 °C, there was no significant (>2%) conversion. At 200 °C, the conversions obtained were very low, being about 2% for 14 min. At 300 °C, 29% conversion of NF_3 was obtained. Conversion dropped quickly to 16% after 35 min. At 400 °C conversion started initially at 92% and dropped to 63% after 50 min.

The XRD patterns revealed that the only crystalline material before heating and reacting the CaO is $Ca(OH)_2$. After reaction the patterns for CaO, $Ca(OH)_2$,

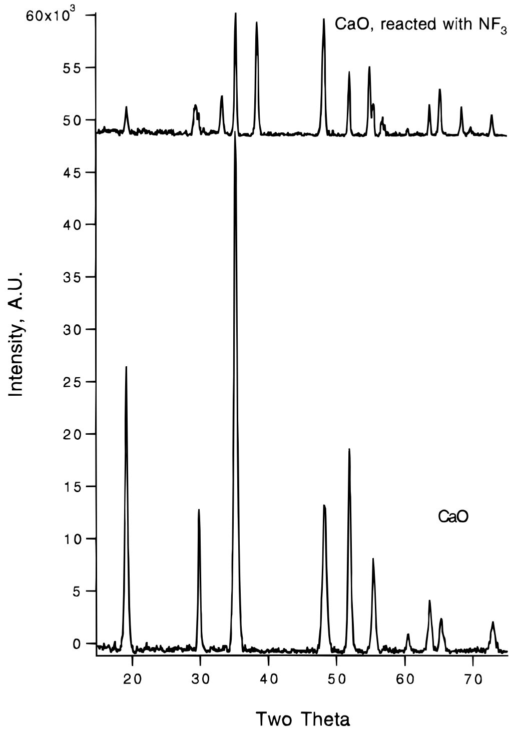

Figure 6. X-ray diffraction pattern for reacted calcium oxide.

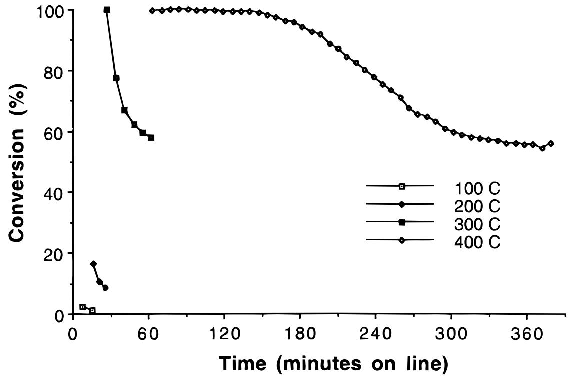

Figure 7. Conversion results for HX zeolite.

and CaF_2 were all observed (see Figure 6 for XRD results).

HX Zeolite. A 0.342 g sample of HX zeolite, with a BET surface area of 155 m^2/g, was reacted with NF_3. At 100 °C there was no significant conversion. At 200 °C the initial and highest conversion was 17%, dropping to 8.6% 10 min later. At 300 °C there was 100% conversion, which immediately began dropping, decreasing to 58% about 35 min later. High conversions (>98%) were obtained at 400 °C for 91 min. Conversion leveled off at 56% at 329 min, and the reaction was terminated at 379 min. Figure 7 shows the conversion results. XRD revealed the presence of amorphous material as a result of the reaction.

Discussion

Alumina Getters. The alumina decomposed NF_3 at 100 °C. However, sustained 100% conversion was not achieved until the temperature was raised to 400 °C. At this temperature the alumina was able to maintain 100% conversion for over 3.5 h. The instantaneous conversion of NF_3 was plotted as a function of time. By integrating the curve, it was found that 68% of the NF_3 passed over the getter was decomposed. The alumina was weighed before and after reaction with NF_3. Assuming a 10% loss in mass due to water (as other alumina samples had shown), the mass increased 146%, from 0.315 g to 0.460 g. The theoretical increase (100% conversion of alumina to Al_2F_6) is a 165% mass increase. Therefore, 146% mass increase represents a 70% conversion of alumina to Al_2F_6, assuming it is the only solid product.

Several factors back up this assumption. No fluorinated gaseous or liquid components were detected in the exit stream, except for NF_3. Al_2F_6 is seen as the only crystalline product using XRD. Thermodynamically, Al_2F_6 is the expected product along with nitrogen oxide gases. Given this assumption, the close agreement of the NF_3 conversion, and the selectivity to Al_2F_6, it is thought that the overall reaction is as follows:

$$Al_2O_3 + 2NF_3 \rightarrow Al_2F_6 + 2NO_x \qquad (1)$$

NO_x's, N_2, and O_2 gases are detected with GC experiments. However, the column used decomposes NO_x gases. It is therefore not possible to determine specific concentrations of the NO_x's in the exit gas.

The reaction was terminated as the conversion of NF_3 fell below 50%. It is believed that the process becomes increasingly mass transfer limited as more and more Al_2F_6 is present.

Na-Doped Alumina Getters. Na-doped alumina was tried, with the expectation that NaF would be formed, as well as Al_2F_6. The surface area of this alumina was lower than that of the undoped material (233 m^2/g as compared to 330 m^2/g for the undoped material), but this cannot account for the much lower activity. At 400 °C, 100% conversion was never achieved, with 98% conversion holding steady for only 20 minutes. The lower activity could be due to pore blockage by the Na, resulting in severe mass-transfer effects. It is possible that the Na was active in decomposing NF_3, forming highly dispersed NaF, which may not be seen with XRD. The major peaks for Al_2F_6 are present, indicating, as with the pure alumina, that aluminum sites play a major role in the decomposition of NF_3.

CaO Getters. A low surface area calcium oxide (lime) was chosen as a getter. It was thought that the stable and nontoxic CaF_2 salt would be a desirable product. Also, lime is very inexpensive and handled easily. Unfortunately, although active initially, CaO was quickly deactivated. Probably as a result of the low surface area, mass transfer effects were greatly exaggerated, and even at 400 °C there was not 100% conversion. The XRD confirms the presence of CaF_2 after reaction, and the GC shows the production of NO_x's.

HX Zeolite Getters. NH_4X zeolite was heated at 350 °C to produce HX zeolite. HX was chosen because it has the highest Al:Si ratio of the common faujasitic zeolites, and previous work has shown that aluminum oxides are more active than silicon oxides in decomposing NF_3. Like the other oxides, there was no sustained activity at 300 °C or below. At 400 °C the zeolite decomposed NF_3 for more than 60 min, making it a better getter than the Na-doped alumina, but not as efficient as the pure alumina. One interesting observation is that the XRD data showed no signs of Al_2F_6 formation, and in fact it was amorphous (HX zeolite decomposes at 400 °C). NO_x's were detected as the major gaseous products.

Conclusion

The general reaction of NF_3 with oxides produces metal fluorides, unidentified NO_x's, and possibly N_2 and/or O_2. No N_2F_4 was detected, despite measures to ensure detection. Activity of the oxides differed considerably, with mass-transport problems appearing to be the major cause of deactivation. Alumina and HX zeolite performed well, but the same alumina doped with Na (8%) and CaO were not as active. It is believed that high surface area may be an important factor in the activity of a particular compound but that the chemical species chosen is more important. For example, in several studies of different silicon oxides[21] it was found that varying the surface area of the silicon oxide from that of a typical quartz tube to >300 m^2/g produced the same conversion results.

Table 3 compares the reactivity of NF_3 with metals and oxides studied previously.[20,22] As can be seen, sustained 100% conversion using any material does not occur until temperatures over 300 °C have been reached. It is believed that the dissociation of NF_3 (which produces NF_2 radicals and becomes significant above 300 °C) is involved in the decomposition of NF_3. This could help explain the rapid drop in conversion at lower temperatures. Also, mass-transfer effects may be more significant at the lower temperatures, especially given the quick residence time of 0.2 s.

Table 3. Comparision of the Activity for Various Oxides and Metals

material	% conv at 300 °C	% conv at 400 °C	ref
silicon	50	100	20
titanium	80	100	20
zirconium	20	100	22
SiO_2	2	89[a]	22
Al_2O_3	85[a]	100	this work
Na-doped Al_2O_3	95[a]	100[a]	this work
CaO	95[a]	100[a]	this work
HX zeolite	100[a]	100	this work

[a] Unsustained conversion (<10 min).

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