The Preparation and Properties of Aluminum Nitride Films

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ABSTRACT

Aluminum nitride films have been deposited on silicon substrates at 800°-1200°C by the pyrolysis of an aluminum trichloride-ammonia complex, $AlCl_3 \cdot 3NH_3$, in a gas flow system. The deposit was transparent, tightly adherent to the substrate, and was confirmed to be aluminum nitride by x-ray and electron diffraction techniques. The deposited aluminum nitride films were found to be polycrystalline with the crystallite size increasing with increasing temperature of deposition. Other properties of aluminum nitride films relevant to device applications, including density, refractive index, dissolution rate, dielectric constant, and masking ability, have been determined. These properties indicate that aluminum nitride films have potential as a dielectric in electronic devices.

Aluminum nitride is a refractory, large energy gap material [sublimation temperature 2400°C (1), energy gap 5.9-6.2 eV (2, 3)] and has chemical, physical, and electrical properties suitable for several applications in electronic devices. For example, its large energy gap, good thermal stability [equilibrium vapor pressure of nitrogen at 1500°C: 0.05 Torr (4)], and chemical inertness [stable in air at temperatures up to 700°C (5)] suggest that aluminum nitride is a good dielectric for active and passive components in semiconductor devices. Aluminum nitride, being a piezoelectric material with a high acoustic velocity, is also well suited for the fabrication of surface wave acoustic devices.

Aluminum nitride has been prepared by several techniques, such as the direct combination of the elements and chemical reactions of gaseous aluminum and nitrogen-containing compounds on substrate surfaces. The direct combination technique requires temperatures in excess of 1500°C (2, 5, 6) and is not suitable for device applications. On the other hand, aluminum nitride films have been deposited on the surfaces of refractory metals, insulators, and semiconductors at considerably lower temperatures by the reaction of aluminum trichloride with ammonia (1, 3, 7-12) and the reaction of trimethylaluminum with ammonia (13). Aluminum nitride films up to 5 μm in thickness have also been deposited on metallic substrates by diode reactive sputtering, and the dielectric properties of sputtered aluminum nitride films were found to be superior to those of bulk polycrystalline material (14). The chemical deposition technique appears to be more compatible with the current device technology; however, the utilization of aluminum nitride in semiconductor devices has not been explored.

In this work, aluminum nitride films have been deposited on single crystal silicon substrates by the pyrolysis of an aluminum trichloride-ammonia complex in a gas flow system. The properties of the deposited films, such as structure, composition, density, refractive index, dissolution rate, dielectric constant, masking ability, etc., have been determined. The experimental methods and results are discussed in this paper.

Preparation of Aluminum Nitride Films

The ammonolysis of aluminum trichloride is commonly used for the deposition of aluminum nitride films. Because of the hygroscopic nature of aluminum trichloride, an aluminum trichloride-ammonia complex was used as the starting material. The complex was prepared by saturating reagent grade anhydrous aluminum trichloride in a fused silica reaction tube with anhydrous ammonia at room temperature. The resulting mass was heated at 350°C in an ammonia flow, and the complex sublimed yielding a white crystalline powder. The composition of the complex, determined by dissolving a weighed amount of the specimen in a known volume of 0.1*N* hydrochloric acid and titrating the excess acid with 0.1*N* sodium hydroxide, was $AlCl_3 \cdot 3NH_3$. This complex is considerably more stable in the laboratory ambient than aluminum trichloride. Its vapor pressure was determined from the extent of vaporization in a sealed silica tube after heating at a predetermined temperature for 24 hr. The vapor pressure data in the temperature range 500°-800°K are shown in Fig. 1; the complex has sufficient vapor pressure at temperatures below 300°C for utilization in the deposition of aluminum nitride. The heat of vaporization of the complex calculated from the slope of this plot was 11.8 ± 0.2 kcal/mole.

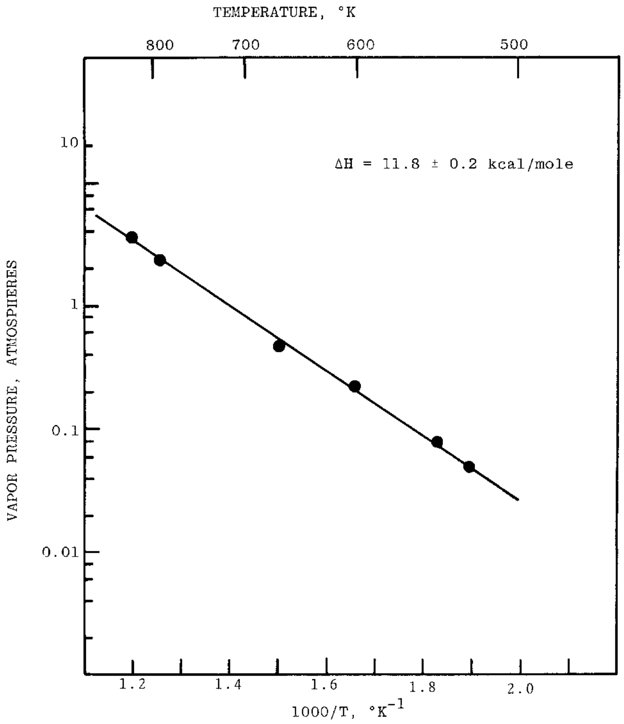

Fig. 1. Vapor pressure of aluminum trichloride-ammonia complex $AlCl_3 \cdot 3NH_3$.

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Key words: aluminum nitride, chemical deposition, electronic devices, silicon.

The deposition of aluminum nitride by the pyrolysis of the aluminum trichloride-ammonia complex in a gas flow system was carried out using an apparatus shown schematically in Fig. 2. The diluent gases used in the deposition process were commercial hydrogen purified by diffusion through a palladium-silver alloy and Matheson anhydrous ammonia of better than 99.99% purity. The reaction tube was made of clear fused silica, 55 mm ID and 3 ft long. A fused silica boat containing the aluminum trichloride-ammonia complex was maintained at 250°C by using an external resistance heater, and hydrogen or a 6:1 hydrogen-ammonia mixture at a flow rate of 30 liters/min was used to carry the complex to the substrate surface. The silicon substrates with main faces of {111} orientation were n-type, 5-20 ohm-cm resistivity, and were mechanically polished and chemically etched in the usual manner. They were supported on a silicon carbide-coated graphite susceptor, and the susceptor was heated externally by an rf generator. Prior to the deposition of aluminum nitride, the substrates were heated at 1150°C in hydrogen for ½ hr to remove the oxide on the surface. In some experiments, the substrate surfaces were etched *in situ* at 1170°C with a hydrogen-hydrogen chloride mixture containing 2% hydrogen chloride. The deposition of aluminum nitride was carried out at substrate temperatures in the range of 800°-1200°C, and the deposition time was usually 15-45 min. The thickness of aluminum nitride films on silicon substrates was determined by removing part of the film and measuring the height of the step generated with a Sloan Dektak and Graphic Chart Recorder.

Under the conditions described above, the deposited films are transparent and tightly adherent to the substrate. The average deposition rates in the temperature range 800°-1200°C are shown in Fig. 3. The deposition rate decreased with increasing temperature from 160 Å/min at 800°C to 120 Å/min at 900°C and 90 Å/min at 1000°C. This decrease of deposition rate is due presumably to the increased contribution of gas phase nucleation at high temperatures. The gas phase nucleation becomes more pronounced at higher concentrations of the aluminum trichloride-ammonia complex in the reactant mixture. For example, films deposited at a rate of 750 Å/min at 900°C had a cloudy appearance as a result of the enhanced gas phase nucleation.

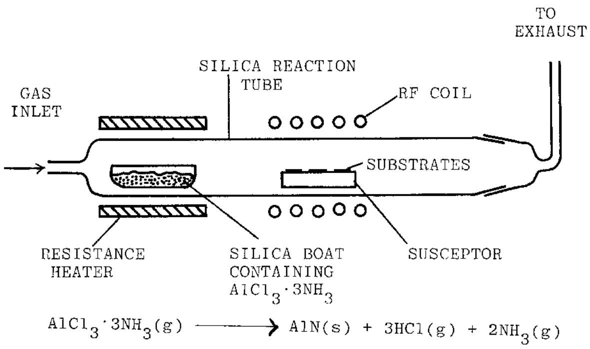

Fig. 2. Schematic of the apparatus used for the deposition of aluminum nitride films.

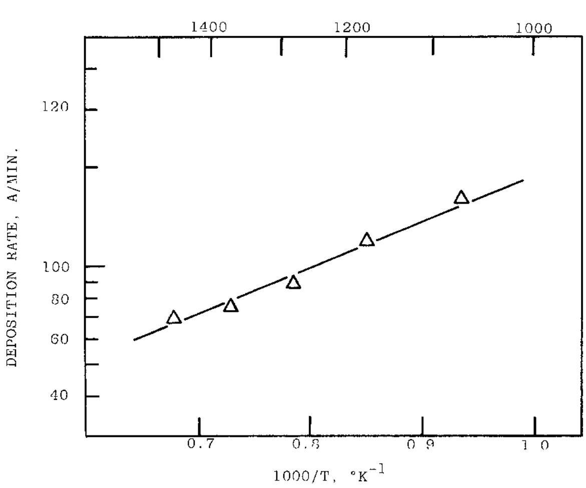

Fig. 3. Average deposition rate of aluminum nitride films as a function of temperature.

The films deposited in the temperature range 800°-1100°C were analyzed by the x-ray diffraction technique. Silicon substrates were removed from the specimens by etching with a nitric acid-hydrofluoric acid mixture, and the resulting material was pulverized and examined by the Debye-Scherrer technique using nickel-filtered CuKα radiation. The diffraction patterns were identical with those reported for aluminum nitride (15), thus confirming that the deposited films were aluminum nitride.

Properties of Aluminum Nitride Films

Structure.—Aluminum nitride films deposited on silicon substrates under proper conditions were uniform, transparent, and highly adherent to the substrate. They showed no structural features when examined with an optical microscope. Several films were investigated by transmission electron microscopy using a Hitachi Model 11BU electron microscope after removing the substrates with a nitric acid-hydrofluoric acid mixture. Figure 4 shows the micrographs of aluminum nitride films deposited in the temperature range 800°-1100°C. All films were polycrystalline, and the average linear dimensions of the crystallites increased with increasing deposition temperature. Typical dimensions of crystallites were 100, 200, 600, 1100, and 2200Å in films deposited at 800°, 900°, 1000°, 1100°, and 1200°C, respectively. This increase in crystallite size with temperature is to be expected. The diffraction patterns of aluminum nitride films deposited at various temperatures are shown in Fig. 5. The d-spacings measured from these patterns further confirm that all films are aluminum nitride. Figure 5

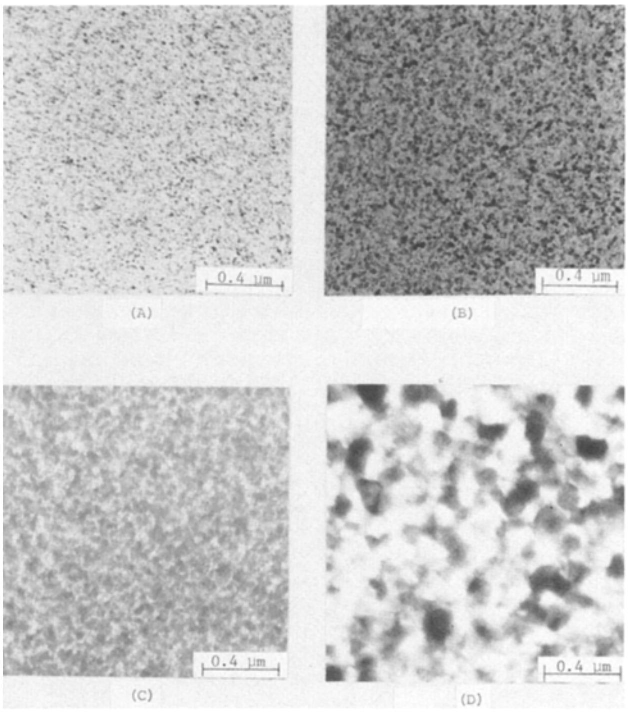

Fig. 4. Transmission electron micrographs of aluminum nitride films deposited at (A) 800°C, (B) 900°C, (C) 1000°C, and (D) 1100°C.

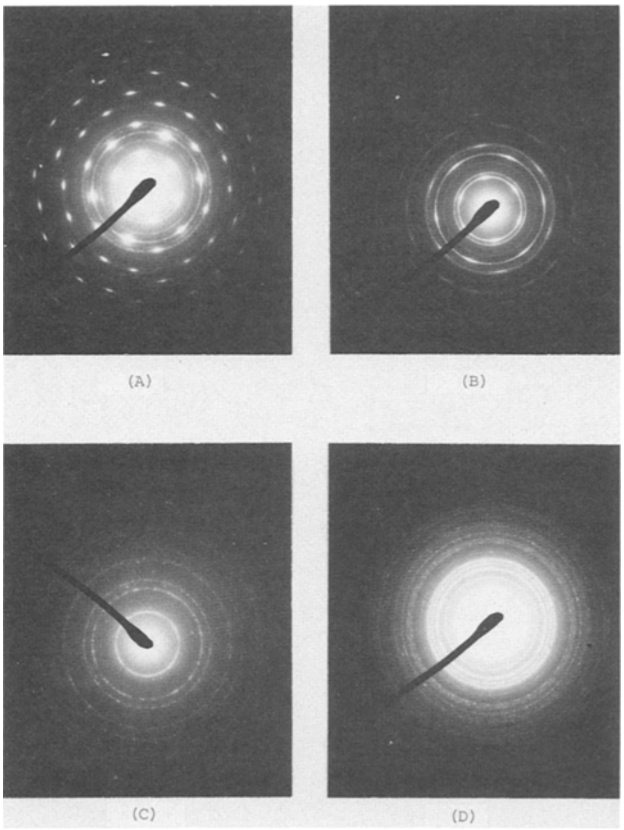

Fig. 5. Electron diffraction patterns of aluminum nitride films deposited at (A) 800°C, (B) 900°C, (C) 1100°C. and (D) 1200°C.

indicates that aluminum nitride films deposited at temperatures above 1000°K are polycrystalline and that preferred orientations are increasingly apparent with decreasing temperature of deposition. The single crystallinity of the substrates appears to have little or no effect on the structural properties of aluminum nitride since aluminum nitride films deposited on the surface of silicon dioxide were essentially the same as those on silicon substrates.

Density, refractive index, and optical absorption.—The density of aluminum nitride films deposited at various temperatures was determined by the floating equilibrium technique using a mixture of 1-bromo 2-iodo benzene and methylene iodide. The temperature of deposition was found to affect only slightly the density of aluminum nitride. Aluminum nitride films deposited at 800°, 900°, 1000°, and 1100°C have densities of 3.15, 3.18, 3.18, and 3.20 ± 0.01 g/cm^3, respectively, as compared with a reported value of 3.13 g/cm^3 (12) and the theoretical density of 3.26 g/cm^3.

The refractive index of aluminum nitride films deposited in the temperature range 800°-1200°C was determined by the Becke line method to be 1.991 ± 0.003, irrespective of the deposition temperature. A few samples were also measured by the ellipsometric technique; the results, though not as reproducible, were usually in good agreement with those by the Becke line method. However, refractive indices as high as 2.17 ± 0.05 have been reported for single crystalline aluminum nitride prepared by the direct reaction of aluminum with nitrogen (16).

The optical absorption spectra of aluminum nitride films deposited under various conditions were taken on a Beckman Model DK-2 spectrophotometer at room temperature. Typical results are shown in Fig. 6, where the thickness of the aluminum nitride film was 18 μm for curve A and 13 μm for curve B. The fundamental absorption edge for all specimens measured was found to be 5.9 ± 0.2 eV, in agreement with that observed by others (2). However, the films deposited at very high rates, 700 Å/min or higher irrespective of deposition temperature, exhibited an additional absorption band in the 3.0 to 3.2 μm region (curve A) while those deposited at low rates, 300 Å/min or lower, showed no absorption in this region (curve B). The absorption in the 3.0-3.2 μm region is presumably due to the N-H or Al-Cl bonds in aluminum nitride films deposited at high rates. As stated previously, the gas phase nucleation becomes pronounced at high deposition rates. The decomposition of the aluminum trichloride-ammonia complex in the gas phase may not proceed to completion, and the deposited material contained N-H or Al-Cl bonds. Thus, the use of low deposition rates is essential for obtaining good quality aluminum nitride films.

Dissolution behavior.—The deposited aluminum nitride films are soluble in phosphoric acid and sodium hydroxide solutions. To determine the dissolute rate of aluminum nitride films, a portion of the specimen was covered with Apiezon Q wax or photoresist, and the specimen was immersed in the etchant with constant agitation for various lengths of time. The dissolution rate was then determined by removing the protective coating and measuring the difference in the step heights using the Dektak system.

The dissolution rate of aluminum nitride films, deposited in the temperature range 800°-1200°C, in a 10% sodium hydroxide solution was determined in the

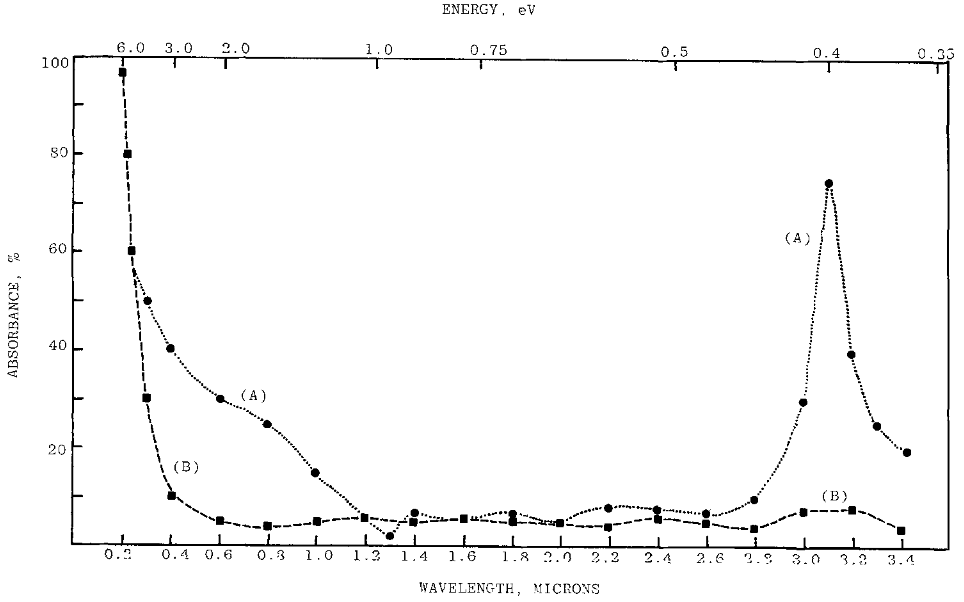

Fig. 6. Optical absorption spectra of aluminum nitride films deposited at a rate of about 700 Å/min (A) and at a rate of about 300 Å/min (B).

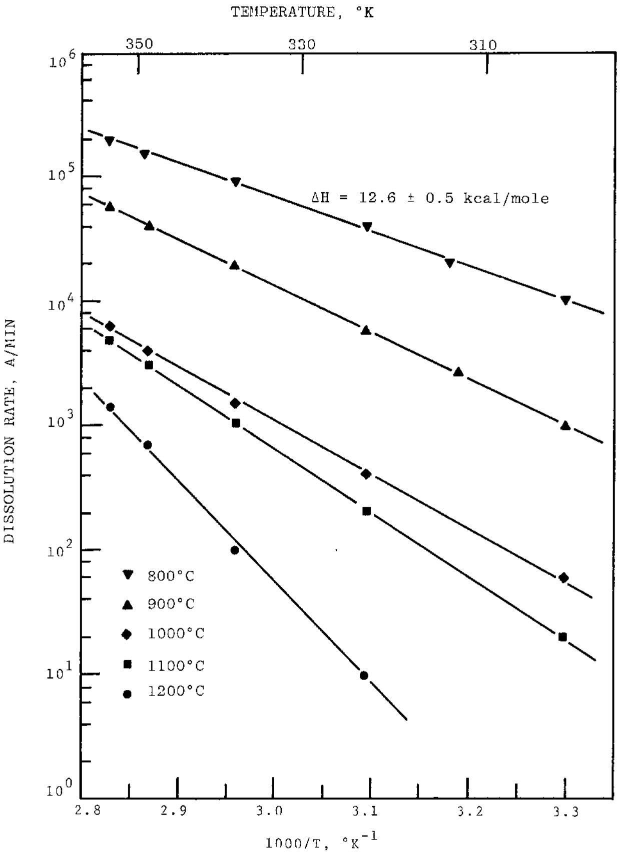

Fig. 7. Dissolution rate of aluminum nitride films, deposited in the temperature range 800°-1200°C, in 10% sodium hydroxide solution.

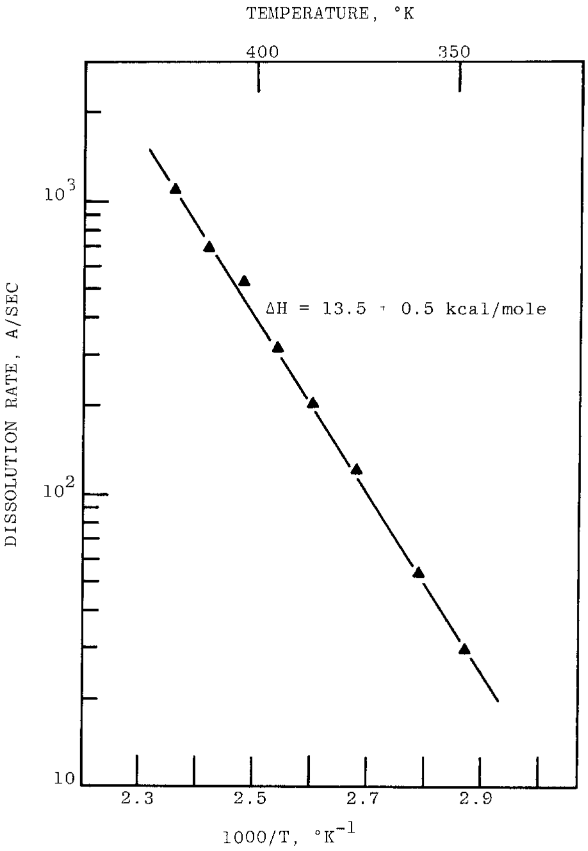

Fig. 8. Dissolution rate of aluminum nitride films deposited at 900°C in 85% phosphoric acid.

temperature range 30°-80°C. The results are shown in Fig. 7. At a given temperature, the dissolution rate of aluminum nitride films decreased with increasing deposition temperature, due presumably to the larger crystallites of aluminum nitride deposited at higher temperatures. Also, the dissolution rate of aluminum nitride films deposited at low temperatures was found to remain the same after annealing at higher temperatures, indicating negligible grain growth. The activation energy of dissolution for aluminum nitride films deposited at 800°C was found to be 12.6 ± 0.5 kcal/mole. The activation energy also increased with increasing deposition temperature. The relatively large activation energy indicates that the dissolution of aluminum nitride films is a surface-reaction controlled process.

The dissolution rate of aluminum nitride films deposited at 900°C was also determined using an 85% phosphoric acid solution. At temperatures up to 50°C, the dissolution rate of aluminum nitride was negligible. Figure 8 shows the dissolution rate in the temperature range 75°-150°C, and the activation energy of this dissolution was found to be 13.5 ± 0.5 kcal/mole, similar to the use of sodium hydroxide solution as an etchant.

Both sodium hydroxide and phosphoric acid solutions used in this work were found to produce clean and structureless surfaces, similar in appearance to the as-grown aluminum nitride films, when examined with an optical microscope.

Masking ability.—To explore the usefulness of aluminum nitride in silicon devices, its capabilities and limitations as masks against the diffusion of boron, phosphorus, aluminum, and gallium into silicon were investigated. Aluminum nitride films of 1000-1700Å thickness, deposited on silicon substrates at 900°C were used in the diffusion experiments. The substrates were n-type, 5-10 ohm-cm resistivity for the diffusion of boron, aluminum, and gallium, and were p-type, 10-20 ohm-cm for the diffusion of phosphorus. The aluminum nitride film was removed completely from circular areas (usually 500 μm diameter) of the specimen by photolithographic techniques using sodium hydroxide or phosphoric acid as an etchant. Sharp, well-defined edges were obtained with virtually no undercutting.

The boron diffusion was carried out by depositing boron oxide glass on the specimen surface at 970°C for 40 min from a boron nitride source followed by redistribution at 1300°C for 1 hr. In the phosphorus diffusion process, phosphorus oxide glass was deposited on the specimen surface at 1000°C for 30 min using phosphorus oxytrichloride as the source, and the redistribution was carried out at 1150°C for 1.5 hr. After the diffusion process, an unmasked region of the specimen was angle-lapped, and the aluminum nitride mask was removed by etching. The resistivity profile on the masked and unmasked regions of the main face and on the beveled surface was measured by the spreading resistance technique (17). The results for the boron diffusion into n-type silicon and the phosphorus diffusion into p-type silicon are shown in Fig. 9. The silicon under the aluminum nitride film was found to have the same conductivity type with essentially no change in resistivity, while p-n junctions were formed in unmasked regions. Thus, aluminum nitride films are successful for masking the diffusion of boron and phosphorus under the conditions used here.

Subsequent to the boron and phosphorus diffusion process, the dissolution rate of the aluminum nitride masks in a 10% sodium hydroxide solution was measured. Aluminum nitride films with boron oxide or phosphorous oxide coatings showed no measurable change in dissolution rate or appearance after heating at 1150°C for 1.5 hr, indicating the inertness of aluminum nitride toward the dopant oxide. However, when the heat-treatment was carried out at 1250°-1300°C after the deposition of boron oxide, the dissolution rate of the nitride films decreased appreciably, indi-

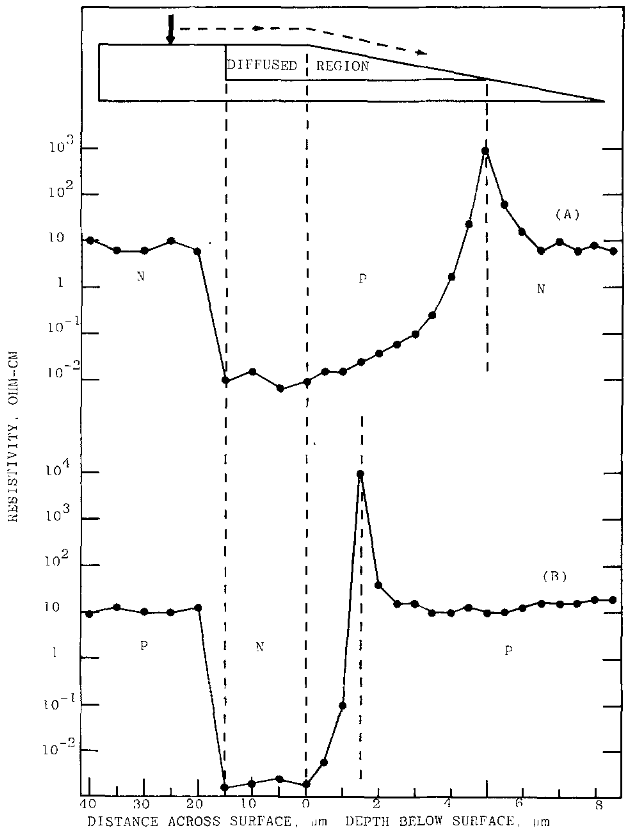

Fig. 9. Resistivity profiles in n-type (A) and p-type (B) silicon specimens after diffusion using aluminum nitride as a diffusion mask.

cating a reaction between aluminum nitride and boron oxide.

The aluminum and gallium diffusions were carried out at 1150°C for 1.5 hr in sealed fused silica tubes using the element as the source material. Aluminum nitride films failed to mask the diffusion of dopant in both cases. This is due presumably to the penetration of aluminum and gallium vapor through the grain boundaries in finely polycrystalline aluminum nitride films at high temperatures.

Dielectric properties.—The dielectric properties of aluminum nitride films were measured at room temperature using aluminum-aluminum nitride-silicon structures. Aluminum contacts of 2.5 × 10^{-2} cm diameter were deposited on aluminum nitride, and ohmic contacts were applied to the back surface of silicon substrates by electroless plating (18).

The dielectric strength of aluminum nitride films deposited in temperature range 800°-1000°C on low resistivity silicon substrates was measured at room temperature using d.c. and 400 kHz. The average dielectric strength of aluminum nitride was found to be 1.5 × 10^7 V/cm for films of 300-400Å thickness, independent of deposition temperature; it decreased to the apparent bulk value of approximately 10^7 V/cm for film thicknesses greater than about 1000Å. Aluminum nitride films deposited at 1100°C or above were found to have lower dielectric strength than those deposited at 800°-1000°C, due presumably to the inclusions in the films of the products of volume reaction where the decomposition of the aluminum trichloride-ammonia complex was not complete. The d-c dielectric strength of aluminum nitride films of 2000Å thickness prepared at 800°-1000°C was also measured at higher temperatures and was found to be approximately 10^7 V/cm at 30°C, 5 × 10^6 V/cm at 100°C, 2.5 × 10^6 V/cm at 200°C, 1.5 × 10^6 V/cm at 250°C, and 10^6 V/cm at 300°C.

Capacitance measurements were made on aluminum-aluminum nitride-silicon structures using a Boonton 75C Direct Capacitance Bridge operated at frequencies up to 0.5 MHz. The insulator capacitance was used to obtain the dielectric constant value. The dielectric constant of aluminum nitride films prepared at 800°, 900°, and 1000°C was found to be 11.5 ± 0.2, and that prepared at 1100°C was considerably lower, usually 8.1 ±0.3, as compared with 9.14 reported for the low-frequency dielectric constant of single crystalline aluminum nitride (19). Also, the dielectric constant of an aluminum nitride film prepared at 800°C was found to remain unchanged after heating at 1100°C in hydrogen for 1 hr, again indicating the structural stability of aluminum nitride. The dielectric constant of all aluminum nitride films prepared in the temperature range 800°-1100°C was found to be independent of frequency and temperature in the ranges 5-500 kHz and 100°-500°K, respectively.

It should be mentioned that the properties of aluminum nitride films discussed above are independent of the nature of the carrier gas, hydrogen or 6:1 hydrogen-ammonia mixture, used in the deposition process.

Summary and Conclusions

Aluminum nitride films have been deposited on silicon substrates at 800°-1200°C in a gas flow system by the thermal decomposition of an aluminum trichloride-ammonia complex, $AlCl_3 \cdot 3NH_3$. This complex was prepared by saturating aluminum trichloride with ammonia and purified by sublimation. The deposit was transparent, tightly adherent to the substrate and was verified by x-ray and electron diffraction techniques to be aluminum nitride. Transmission electron microscopy indicated that all aluminum nitride films were polycrystalline; the crystallite size increased with increasing temperature of deposition, and the preferred orientations became more apparent at lower deposition temperatures.

At deposition temperatures in the range of 800°-1000°C, the average density, refractive index, dielectric strength, and dielectric constant of aluminum nitride were found to be 3.18 g/cm^3, 1.99, 10^7 V/cm, and 11.5, respectively. Aluminum nitride films are soluble in sodium hydroxide and phosphoric acid solutions, and the standard photolithographic technique can be readily applied. Aluminum nitride films were found to be capable of masking against the diffusion of boron and phosphorus into silicon from the oxide sources. These properties indicate that aluminum nitride films have great potential as a dielectric in solid-state devices.

Acknowledgment

This research was supported by the Langley Research Center of the National Aeronautics and Space Administration under Grant NGL 44-007-042.

Manuscript submitted Feb. 6, 1974; revised manuscript received March 12, 1975.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1976 JOURNAL. All discussions for the June 1976 Discussion Section should be submitted by Feb. 1, 1976.

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Technical Notes

Vapor Deposition of Sulfur-Doped GaAs Layers

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Sulfur is a commonly used dopant in the vapor growth of n-type GaAs epitaxial layers (1-7). The most straightforward approach is to use H_2S as a vapor dopant. This gas can be purchased diluted with hydrogen and bled into the deposition system using a variable leak. However, it appears to be difficult to obtain well-defined and reproducible dopant concentrations due to irreversible changes of the leak rates. Experiments have shown that the variable leaks (Varian, Leybold) commonly used in vacuum systems are calibratable only to within an order of magnitude. Another alternative, the stepwise dilution of the doping gas by using fine metering valves and ball flowmeters requires an extensive apparatus and time-consuming calibration also. These problems are most likely responsible for the large discrepancies in the literature data regarding the relationship between the H_2S concentration in the gas phase and the donor concentration in the epitaxial film (5, 6).

Other workers have used solid sulfur as a primary source (2, 7). The element can be vaporized into the reactor either directly or via an H_2S generator. A drawback of this method results from the difficulties in evaporating sulfur powder or grains with a well-defined vapor pressure. Both the evaporating surface area and the crystalline form and hence the vapor pressure of the sulfur may change during heat-treatment.

In the present investigation we have attempted to find improved sulfur doping methods and to clarify the discrepancies referred to above. This was accomplished by using a capillary for the controlled injection of H_2S or by adding a liquid sulfur compound to the $AsCl_3$ bubbler in the deposition system.

The H_2S doping experiments were carried out in a standard apparatus (8) for the $Ga/AsCl_3/H_2$ process (9). Well-defined concentrations of H_2S were added to the gas stream by controlling, via a reducing valve, the input pressure to a capillary tube of $\approx 150\ \mu m$ diameter and 6 cm length used for injecting the doping gas into the hydrogen carrier. The system was calibrated by determining the time required to pass a defined amount of gas through the capillary at a given input pressure. The doping gas was a mixture of H_2S (985 ppm) in H_2, bottled in a steel cylinder.

For the second approach S_2Cl_2 was selected as a liquid sulfur dopant source. This compound appears to fulfill the main requirements for use in this application: (*i*) It can be obtained in a relatively pure form. (*ii*) It will decompose at the deposition temperature. (*iii*) In the working temperature range of the $AsCl_3$ source (15°-25°C) its vapor pressure is such that expitaxial layers in the 10^{16}-10^{17} cm^{-3} doping range can be obtained.

The data in Fig. 1 show that the partial pressures of $AsCl_3$ (10) and S_2Cl_2 (11) are equal within approximately 10% around room temperature. Making the likely assumption that the two liquids form an ideal mixture, the ratio of their partial pressures in the vapor phase will be nearly the same as the ratio of their concentrations in the $AsCl_3$-bubbler.

For the S_2Cl_2 doping experiments a reactor was used with two Ga source tubes side by side, each connected to a bubbler, one for $AsCl_3$, the other for the $AsCl_3$-S_2Cl_2 mixture (Fig. 2). In the deposition zone the dopant concentration can be varied either by varying the proportion of the gas streams through the two bubblers or by changing the amount of S_2Cl_2 in the $AsCl_3$ bubbler. The results indicate that after saturation of the Ga source with As along with formation of a GaAs crust (12) a constant sulfur pressure is obtained in the system, and steady-state conditions can be expected during expitaxial growth.

The following starting materials were used: chromium-doped GaAs substrates ($\rho = 10^7$-10^8 ohm-cm, Monsanto) orientated 2° off $\{100\}$ towards $\{110\}$, gallium (99.9999% Johnson Matthey), $AsCl_3$ (Suprapur, Merck), S_2Cl_2 (99%, Riedel-de Hean) redistilled, H_2S (985 ppm in H_2, Matheson). The hydrogen was purified in a Pd-diffuser.

The experimental results in Table I demonstrate the behavior of the deposition system using S_2Cl_2. The epitaxial layers were grown in the listed succession, at a deposition temperature of 740°C, a flow rate of 200 ml/min (tube diameters: source tube 25 mm, substrate tube 55 mm), and an $AsCl_3$-partial pressure of $9.9 \cdot 10^{-3}$ atm. The deposition time was 1 hr. An amount of 5 μl of S_2Cl_2 was added to 100 ml of $AsCl_3$, giving a doping level of $3.4 \cdot 10^{16}$ cm^{-3} determined by Hall effect measurements. By transferring the Ga source into the second source tube connected to the bubbler containing only $AsCl_3$ a doping level of $2.3 \cdot 10^{15}$ cm^{-3} was reached under the same growth con-

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Key words: GaAs, epitaxy, sulfur doping, gas phase deposition.