Temperature dependence of the sticking probability and molecular size of the film growth species in an atmospheric chemical vapor deposition process to form AlN from $AlCl_3$ and NH_3

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(Received 4 June 1991; accepted for publication 19 August 1991)

The sticking probability and molecular size of the growth species were determined as a function of deposition temperature ranging from 700 to 950 °C, in the AlN films prepared from $AlCl_3$ and NH_3. A novel method was developed, that includes the measurement of the film thickness profile on micron-sized trenches and the molecular diffusivity of the growth species. The molecular size was about 1 nm at 700–850 °C and decreased gradually with increasing temperature. The sticking probability increased from 0.02 to 0.5 in the temperature range 700–950 °C and, surprisingly, obeyed the Arrhenius law in spite of this large probability of sticking. The activation energy amounted to 136 kJ/mol.

Increasing interests have been paid to the growth species in the film preparation processes including chemistry. The growth species in the chemical vapor deposition (CVD) processes can be a gaseous reactant itself or an intermediate product formed in the gas phase. The contribution of various chemical species in the preparation of silicon-related films has extensively been discussed.[1,2] However, little is known about this for the other systems, particularly, in AlN synthesis. In our recent study, it was suggested that the cluster having a molecular size around 1 nm is the growth species in the atmospheric chemical vapor deposition (APCVD) of AlN from $AlCl_3$ and NH_3. In parallel to the effort to identify the chemical structure of the growth species, attempts were made to determine its sticking probability on the surface of a film. A direct experimental method is to divide the film growth rate by the known concentration of the growth species.[3,4] Also, a microtrench method can effectively be used to determine the sticking probability, that includes observation of the trench coverage profile by scanning electron microscopy and comparison of the profile with a model prediction.[5–7] This method can be applied even to a system in which the growth species is not identified chemically. The present study combines this second method with the molecular size information obtained from the diffusion coefficient data taken in a same experimental run, to determine simultaneously the sticking probability and molecular size of the growth species.

A flow type of APCVD system was used. The reactor was a quartz tube 2 to 10 mm inner diameter and 1 m long, equipped with an electric furnace. The concentrations of $AlCl_3$ and NH_3 were kept constant at 0.4 and 8 mol%, respectively. The substrate was a silicon wafer having microtrenches constructed by normal lithographic procedures, and was placed in the isothermal zone of the reactor tube. Figure 1 shows the film thickness profiles on the micron sized trenches observed by scanning electron microscopy. The experiments were carried out at different temperatures. The film is thicker near the open mouth of the trench than near the bottom of it. With increasing temperature, the difference between the thickness on the top and that at the bottom becomes larger.

The concentration gradient of the film growth species along the depth of the trench is conceivably responsible for the film thickness profile, and it is enhanced by the consumption of the growth species during penetration. The observed temperature dependence indicates, therefore, that the sticking probability of the growth species increases with increasing temperature.

An attempt was made to evaluate the sticking probability from the film thickness profile by deriving a theoretical relation of a profile to a sticking probability. Under the condition considered, the mean free path of a molecule is approximately 0.1-μm, that is smaller than the trench dimension by an order. Molecular diffusion, therefore, dominates the penetration process of the growth species into the trench.

Molecular kinetic theory relates the growth rate to the sticking probability, η, by

$$\text{growth rate} = \frac{\eta V_t}{4 - 2\eta} C \qquad (1)$$

where C is the concentration of the growth species and V_t is its thermal mean velocity expressed by

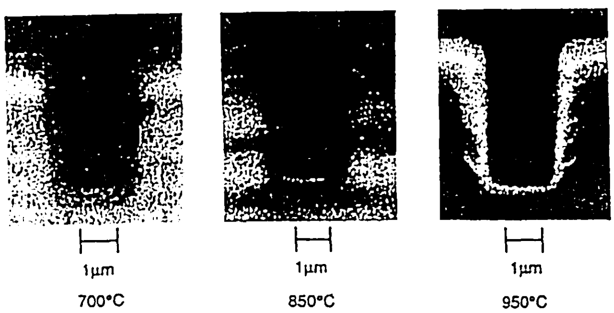

FIG. 1. SEM micrographs showing step coverage of AlN film deposition on silicon wafer having a microtrench with 2.6 μm width and 3.62 μm depth at temperature 700, 850, and 950 °C.

TABLE I. Parameters for calculation of sticking probability.

	700 °C	750 °C	800 °C	850 °C	900 °C	950 °C
Step coverage (T_b/T_s)	0.90	0.78	0.63	0.52	0.44	0.26
Aspect ratio (L/W)	1.98	2.0	2.0	1.3	1.4	1.36
Dimensionless number (Φ)	0.38	0.65	0.86	0.95	1.15	1.54
Diffusivity (D, m^2/s)	1.20×10^{-4}	1.23×10^{-4}	1.55×10^{-4}	1.81×10^{-4}	2.44×10^{-4}	4.08×10^{-4}
Molecular diameter (Å)	9.9	10.0	9.4	9.0	7.6	5.6
Molecular weight (M,g/mol)	450	460	385	328	204	82
Thermal velocity (V_t,m/s)	217	223	238	289	353	570
Sticking probability (η)	2.42×10^{-2}	6.87×10^{-2}	1.22×10^{-1}	2.17×10^{-1}	3.19×10^{-1}	5.29×10^{-1}

$$V_t=\sqrt{8kT/M} \tag{2}$$

where k is the Boltzmann constant, T is temperature, and M is the molecular weight. Neglecting the concentration gradient in a plane perpendicular to the trench depth, the change in the trench geometry during film deposition, and the gas phase reaction inside the trench reduces the governing equation into a simple form,

$$D\frac{d^2C}{dx^2}=\frac{2}{w}\frac{\eta V_t}{4-2\eta}C \tag{3}$$

where x is a coordinate along the trench depth, D is a diffusivity, and W is a trench width. The boundary conditions are

$$D\frac{dC}{dx}=\frac{\eta V_t}{4-2\eta}C, \quad \text{at } x=0, \tag{4}$$

$$C=C_0 \quad \text{at } x=L \tag{5}$$

where L is a trench depth. Solving Eq. (3) with the boundary conditions gives the concentration profile that is equivalent to the growth rate profile. In turn, the ratio of the film thickness at the bottom of a trench (T_b) to that at the top (T_s) is obtained,

$$\frac{T_b}{T_s}=\frac{(\eta V_t/4-2\eta)\ C_{x=0}}{(\eta V_t/4-2\eta)\ C_{x=L}} =\frac{1}{\cos h(\Phi)+\frac{1}{2}(W/L)\Phi\sin h(\Phi)} \tag{6}$$

where Φ is a dimensionless number defined as

$$\Phi=L\sqrt{\frac{2\eta V_t}{(4-2\eta)DW}}. \tag{7}$$

Rearranging Eq. (7) yields an equation to calculate η.

$$\eta=\frac{2\Phi^2DW}{\Phi^2DW+L^2V_t}. \tag{8}$$

The values of Tb/Ts and Φ at various temperatures are shown in Table I. The molecular diffusion coefficient D and thermal mean velocity V_t of the growth species are required to obtain η from Eq. (8).

In the case of a tubular reactor, the overall rate of the film growth was found to be governed by diffusion of the growth species from the stream to the inner wall of the reactor. Consequently, the molecular diffusivity of the growth species could be obtained from the longitudinal growth rate profile in the reactor tube. Only the results are shown in Table I. Details of the analytical procedure will be described elsewhere.[8]

Comparing the diffusivity with the Chapman–Enskog equation gives the collision cross section of the species that can be converted into a diameter of an equivalent sphere.[9] Figure 2 shows the results. The diameter is about 1 nm at 700–850 °C and decreases gradually with increasing temperature.

Calculation of V_t from Eq. (2) requires the molecular weight M. We assumed the chemical formula of $[(AlN)(HCl)_x]_n$ to determine the density of the growth species according to the Schroeder method.[10] The molecular weight M, which was estimated from molecular diameter and density, depended only slight on the value of x, even if x changed from 0 to 3. For example, the molecular weight of 1 nm cluster was 450 g/mol for $x=0$ and increased to 460 g/mol for $x=3$. The number of AlN unit composing a growth species, n, is 4 at $x=3$ and 11 at $x=0$. Whatever the chemical composition is, the growth species should be a cluster.

The value of D and V_t was substituted into Eq. (8) to determine the sticking probability. Figure 3 gives the results in terms of η versus $1/T$. The activation energy corresponding to the straight line amounts to 136 kJ/mol. An Arrhenius law is believed to hold true only when a very small fraction of a group of numbers of molecules in thermal equilibrium can pass a potential barrier. In this sense, it is very surprising that a sticking process having a prob-

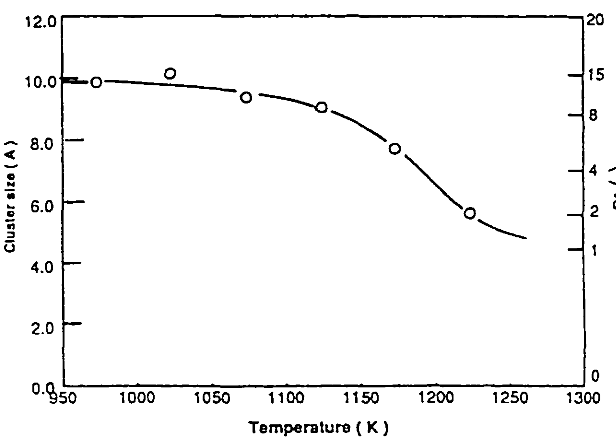

FIG. 2. Temperature dependence of cluster size.

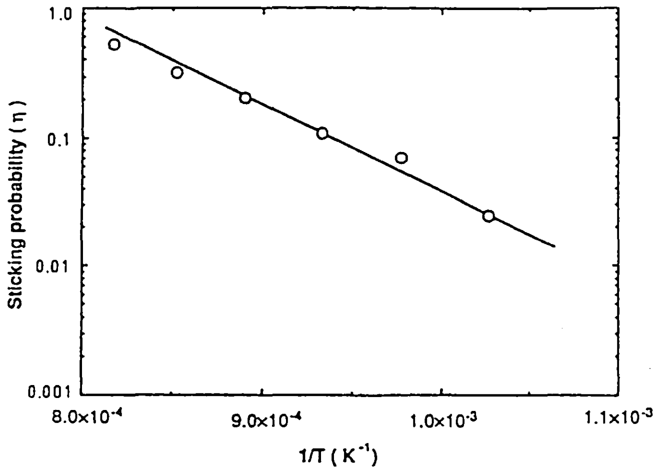

FIG. 3. Arrhenius type plot of reactive sticking probability at a temperature range from 700 to 950 °C.

ability close to unity ($0.02 < \eta < 0.5$) obeys an Arrhenius law. The mechanism is to be studied further.

In conclusion, the growth species in the formation of AlN films by the APCVD process from $AlCl_3$ and NH_3 in a temperature range 700–850 °C is a cluster having a size around 1 nm. The sticking probability of the growth species increases from 0.02 to 0.5 in the temperature range 700–950 °C and obeyed Arrhenius type temperature dependency. The activation energy is 136 kJ/mol.

The authors greatly appreciate the help of Dr. K. Sugawara, Hitachi VLSI Engineering Corp., in supplying the fabricated silicon wafers.

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