

Heterogeneous nucleation and growth of polycrystalline silicon

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Abstract. The heterogeneous nucleation theory of silicon on SiO_2 and Si_3N_4 substrates has been developed using classical theory. It is shown that the experimental observations can be explained on the basis of the bond energies of O–H, N–H and Si–H. A reaction model is proposed for the growth of silicon on silicon from silane, using hydrogen as a carrier gas in the temperature region 600–900°C. The growth rate of silicon is shown to be equal to $P_{\text{SiH}_4}/P_{\text{H}_2}$ when the partial pressure of hydrogen is high, and is independent of the total pressure and the partial pressure of hydrogen in the lower region.

Keywords. Silicon layer; heterogeneous nucleation; SiO_2 and Si_3N_4 substrates; growth rates; step-kink.

1. Introduction

Polycrystalline silicon layers are extensively used in the electronics industry. Gas phase reactions in silicon epitaxial growth have been studied widely by a number of authors and reaction models deduced from an equilibrium view point (Sladek 1971; Bloem 1970; Bylander 1962). However, the actual reaction is not in equilibrium, but rather quasi-equilibrium (Aoyama *et al* 1981). In the first part of this paper we present the heterogeneous nucleation phenomena of silicon on SiO_2 and Si_3N_4 substrates as a function of temperature using the classical nucleation theory (Sigsbee 1969; Dhanasekaran and Ramasamy 1982). In the second part we propose a model for the growth of silicon layers on silicon from silane as a function of temperature and at different total pressures, with and without hydrogen, based on the growth process described by Kossel and Stranskii (Mullin 1972; Strickland-Constable 1968) where adatoms arrive at the surface and diffuse to kink sites where they are incorporated in the crystal lattice (Dhanasekaran and Ramasamy 1981; Hartman 1973). Burton *et al* (1951) have given the mathematical and physical frame work to calculate the kinetics of crystal growth.

The expressions for the equilibrium concentration of critical nuclei of silicon on SiO_2 and Si_3N_4 substrates have been established and taking into account the O–H, N–H and Si–H bond energies, the different behaviour of the silicon nucleus on the SiO_2 and the Si_3N_4 substrates can be explained qualitatively. It is found experimentally that the behaviour of equilibrium concentrations of the silicon nucleus on the SiO_2 substrate increases with temperature in the range 600–900°C, while beyond 900°C it tends to decrease, whereas the concentration of silicon on the Si_3N_4 substrate is found to decrease with increase of temperature. At high temperatures the growth rate of

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silicon is determined by gas phase diffusion of the reactant to the growing interface and at low temperatures surface reactions determine the growth rate, independent of the magnitude of the total pressure. In the present investigation the growth rate of silicon on silicon from silane, using hydrogen as a carrier gas, is evaluated in the temperature range 600–900°C by considering a reaction scheme including the dissociation of SiH_4 into SiH_2 , adsorption of SiH_2 on the lattice, surface diffusion of SiH_2 to the free step and then to the kink site. It is observed that the growth rate of silicon is proportional to the ratio of the partial pressure of SiH_4 to that of H_2 in the case of the partial pressure of H_2 exceeding 10^{-2} bar. If the partial pressure of H_2 is low, then the growth rate is independent of the total pressure and the partial pressure of hydrogen.

2. Nucleation of silicon on SiO_2 and Si_3N_4 substrates

According to the classical heterogeneous nucleation theory, the balance of the cohesion between the silicon atoms in the cluster and the adhesion between silicon and foreign substrate determines the shape of the nucleus. For high adhesion energy the nucleus will spread on the foreign substrate, for high cohesive forces the nucleus will have a more or less spherical shape which resembles that for homogeneous nucleation (Bloem and Giling 1978).

The net free energy change upon the formation of a cap-shaped silicon embryo on the substrate, taking into account the net interfacial energy terms and the volume free energy change is (Sigsbee 1969)

$$\Delta G = -\frac{4}{3}\pi r^3 \left(\frac{kT}{v} \ln \frac{p}{p_0} \right) [(2 - 3 \cos \theta + \cos^3 \theta)/4] + 4\pi r^2 [(1 - \cos \theta)/2] \sigma_{gn} + \pi r^2 \sin^2 \theta (\sigma_{sn} - \sigma_{sg}), \quad (1)$$

where r is the radius of the silicon embryo, $kT \ln p/p_0$ is the supersaturation function, σ_{gn} , σ_{sn} and σ_{sg} are the interfacial forces between nucleus and gaseous phase, substrate and nucleus, and substrate and gaseous phase, respectively, and θ is the contact angle. For the critical nucleus, the free energy of formation is

$$\Delta G^* = \frac{16\pi\sigma_{gn}^3 v^2}{3(kT \ln p/p_0)^2} \phi(\theta), \quad (2)$$

where

$$\phi(\theta) = (2 - 3 \cos \theta + \cos^3 \theta)/4. \quad (3)$$

The epitaxial position of the nucleus will have a smaller contact angle θ on the foreign substrate and consequently a lower value of the energy of formation of the nucleus. This formation energy in turn strongly depends on the supersaturation. This leads to a relation between incoming flux, substrate temperature and nucleation behaviour. The concentration of the critical nuclei having n^* silicon atoms formed on the substrate is given by

$$\frac{C(n^*)}{C_s} = \left(\frac{C(1)}{C_s} \right)^{n^*} \exp(-\Delta G^*/kT), \quad (4)$$

where C_s is the number of sites on the substrate and $C(1)$ is the monomer concentration.

The above classical nucleation theory is used to explain qualitatively the nucleation

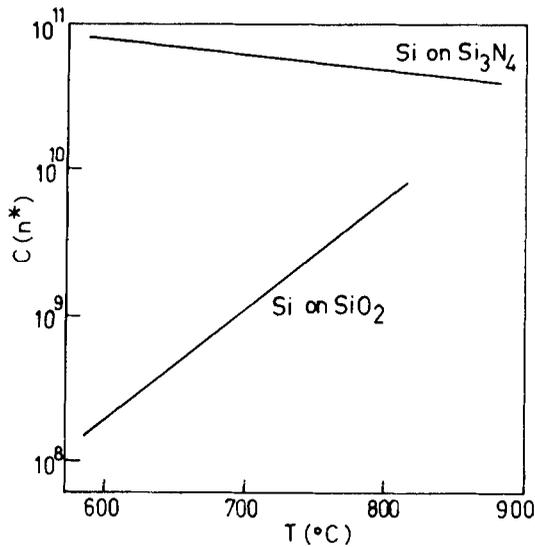


Figure 1. Typical experimental variation of the equilibrium concentration of the silicon nucleus as a function of temperature for silane, using hydrogen as a carrier gas, on SiO₂ and Si₃N₄ substrates.

behaviour of silicon on SiO₂ and Si₃N₄ substrates. Figure 1 shows the experimental observations of typical variation of silicon cluster concentration with substrate temperature for silane in hydrogen as a carrier gas on SiO₂ and Si₃N₄ substrates in the range 600–900°C (Claassen and Bloem 1981). It can be observed that the concentration of silicon nuclei on SiO₂ substrates increases with increasing temperature whereas the density of silicon clusters on Si₃N₄ substrates decreases in the temperature range of 600–900°C using hydrogen as the carrier gas. The difference in nucleation behaviour of silicon between SiO₂ and Si₃N₄ substrates is explained by a strong adsorption of atomic hydrogen on the SiO₂ substrate. Since the difference between the O–H (102 kcal/mole) and the N–H bond energies (83 kcal/mole) is about 20 kcal/mole (JANAF Tables 1971), the energy of formation of the silicon nucleus on the SiO₂ substrate is very different from that of the silicon cluster on Si₃N₄ substrate. More theoretical work is required to compare the observed experimental results quantitatively.

3. Growth of silicon layers from silane

In the temperature range of 600–900°C, the growth of silicon is limited by a chemical or surface controlled process. It is assumed for the low temperature growth of silicon that adatoms arriving at the step, diffuse to kinks which are present on the step with a velocity sufficiently high to assure an uninterrupted lateral movement of the steps (Bloem and Giling 1978). If the chemical reaction is rapid then a general model remains in which silicon adatoms diffuse over the surface to steps and along the step to a stable kink position (Dhanasekaran 1984). Reactions such as adsorption, desorption, surface diffusion to the step and then one-dimensional diffusion to the kink involve activation

energy. The growth rate R resulting from these processes can be described by the expression

$$R \propto \exp(-\Delta H/R_g T), \quad (5)$$

where ΔH is the apparent activation energy for the processes, R_g is the gas constant and T is the absolute temperature. According to our scheme of reaction, the total activation energy can be assumed to be made up of five parts, i.e.,

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5, \quad (6)$$

where ΔH_1 , ΔH_2 , ΔH_3 , ΔH_4 and ΔH_5 are the activation energies associated with the dissociation of SiH_4 in the gaseous phase, adsorption, surface diffusion to the free step, diffusion to the kink site and growth of silicon layers respectively. The total activation energy for the growth of silicon from silane in hydrogen as carrier gas is about 40 kcal/mole (Claassen and Bloem 1981).

A reaction scheme will be presented in the following including the dissociation of SiH_4 to SiH_2 , adsorption of SiH_2 on the lattice, surface diffusion of SiH_2 to the free step and then to kink site to explain the experimental observations. The following sequence of steps are taken into account:

(i) The dissociation reaction in the gaseous phase



The heat of reaction (ΔH_1) for the above reaction is 52 kcal/mole (Newman *et al* 1979).

(ii) Adsorption of SiH_2 on a free surface site



where $*$ denotes a free site on the surface. The heat of adsorption of SiH_2 on the silicon surface is approximately -73 kcal/mole (Chernov 1977). From (7) and (8), the concentration of SiH_2 is

$$[\text{SiH}_2] = p_{\text{SiH}_4} k_1 / \{k_{-1} p_{\text{H}_2} + k_2 [*]\}. \quad (9)$$

(iii) Surface diffusion of SiH_2 to a free step site $*$ (step)



Heat of above reaction is about -73 kcal/mole. The concentration of SiH_2^* is

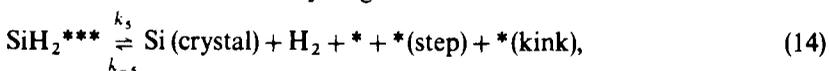
$$[\text{SiH}_2^*] = [\text{SiH}_2][*] k_2 / \{k_{-2} + k_3[*(\text{step})]\}. \quad (11)$$

(iv) Diffusion to the free kink site $*$ (kink)



$$[\text{SiH}_2^{**}] = [\text{SiH}_2^*][*(\text{step})] k_3 / \{k_{-3} + k_4[*(\text{kink})]\}. \quad (13)$$

(v) Growth of silicon and release of hydrogen



$$[\text{SiH}_2^{***}] = [\text{SiH}_2^{**}][*(\text{kink})] k_4 / \{k_{-4} + k_5\}. \quad (15)$$

The $[\text{SiH}_2^{***}]$ can be calculated by assuming the steady state conditions. Using the assumptions that $k_4 \ll k_{-3} \ll k_2$, $k_3 [^*(\text{step})] \ll k_{-2} \ll k_1$ and $k_5 \ll k_{-4}$ and from (9), (11), (13) and (15), one can get

$$[\text{SiH}_2^{***}] = \frac{k_1 k_2 k_3 k_4 p_{\text{SiH}_4} [^*] [^*(\text{step})] [^*(\text{kink})]}{(k_{-1} p_{\text{H}_2} + k_2 [^*]) k_{-2} k_{-3} k_{-4}}. \quad (16)$$

With $k_i/k_{-i} = C_i \exp(-\Delta H_i/R_A T)$ (Claassen and Bloem 1985), (16) can now be rearranged as

$$[\text{SiH}_2^{***}] = C_1 C_2 C_3 C_4 \frac{p_{\text{SiH}_4} [^*] [^*(\text{step})] [^*(\text{kink})]}{p_{\text{H}_2} + (k_2 [^*]/k_{-1})} \times \exp\{-(\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4)/R_A T\}. \quad (17)$$

The growth rate of silicon is given by

$$R = C_5 [\text{SiH}_2^{***}] \exp(-\Delta H_5/R_A T). \quad (18)$$

Incorporating the value of $[\text{SiH}_2^{***}]$ from (17) in (18), the growth rate becomes

$$R = \sum_{i=1}^5 C_i \frac{p_{\text{SiH}_4} [^*] [^*(\text{step})] [^*(\text{kink})]}{p_{\text{H}_2} + (k_2 [^*]/k_{-1})} \exp\left(-\sum_{i=1}^5 \Delta H_i/R_A T\right). \quad (19)$$

It is observed in (19) derived above that the growth rate of silicon from silane is proportional to $p_{\text{SiH}_4}/p_{\text{H}_2}$ when hydrogen is present in the carrier gas and $k_2/k_{-1} < p_{\text{H}_2}$. In the temperature region of 600–900°C, the partial pressure of hydrogen is found to have a pronounced influence. Figure 2 shows the typical experimental variation of the

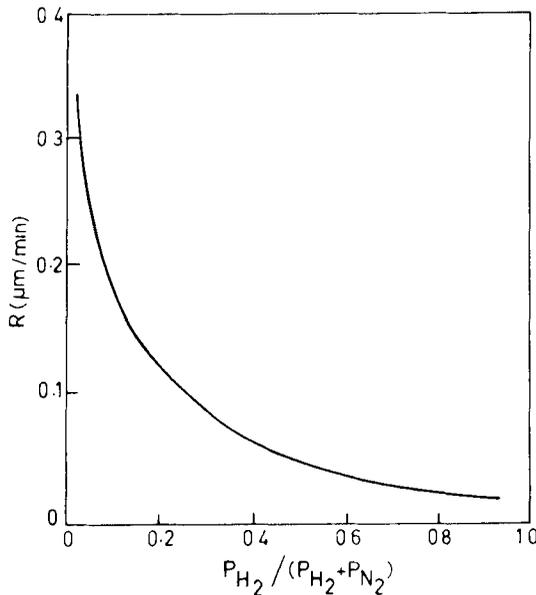


Figure 2. Experimental variation of the growth rate of silicon at 700°C, for 0.2 volume percent silane and different mixtures hydrogen and nitrogen at atmospheric pressure (Claassen and Bloem 1981).

growth rate of silicon at 700°C for an input concentration of 0.2 volume percent silane and different mixtures of hydrogen and nitrogen (Claassen and Bloem 1981). A high growth rate of silicon in inert ambients is observed, much higher than in hydrogen. Therefore, if the partial pressure of hydrogen is zero or very less, the growth rate in inert gas is much larger than in hydrogen. As discussed above, in the temperature range of 600–900°C, the growth of the silicon layers is the surface controlled reaction and the apparent activation energy (≈ 40 kcal/mole) is almost independent of the partial pressure of hydrogen. In the present model, the best fit of the experimental data can be expected in the low temperature region with small temperature dependence of k_2/k_{-1} combined with a concentration of free surface sites and free step sites almost equal to the total number of sites. Based on the reaction scheme given above, an evaluation of ΔH_4 and ΔH_5 can be made, giving $\Delta H_4 + \Delta H_5 \approx 130$ kcal/mole.

4. Conclusion

The nucleation of silicon on SiO_2 and Si_3N_4 substrates has been qualitatively studied using the classical heterogeneous nucleation theory. The experimental observations of silicon nuclei on SiO_2 substrates which increase with increasing temperature while decreasing on Si_3N_4 substrates, using hydrogen as a carrier gas is explained on the basis of the relative bond strengths of the O–H (102 kcal/mole), N–H (83 kcal/mole) and Si–H bonds (70 kcal/mole).

In the temperature region, 600–900°C, the surface reactions determine the growth rate of silicon, which decreases with increasing hydrogen partial pressure giving

$$R \propto p_{\text{SiH}_4} / \left(\frac{k_2[\ast]}{k_1} + p_{\text{H}_2} \right).$$

For values of the partial pressure of hydrogen exceeding 10^{-2} bar, the growth rate of silicon is directly proportional to $p_{\text{SiH}_4}/p_{\text{H}_2}$.

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