화학 증착법에 의한 규소 박막 구조의 내부 조건과 grain 평균 크기의 이론적 전개

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Intrinsic Phase Boundary and Average Grain Size for Silicon CVD

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1. Introduction

It is well known that the crystalline nature of deposited film depends on deposition conditions, mainly on temperature and partial pressure of a source gas(es). It is not clear, however, under what conditions a particular crystalline structure, i.e. amorphous, polycrystalline, and monocrystalline, results. Because of the importance of silicon, several attempts have been made for silicon depostition to delineate the regions in which a particular crystalline structure is favored. Bloem attempted to define the boundary between mono- and poly-crystalline structure solely in terms of growth rate and temperature. Joubert et al. attempted to group different crystalline structures obtained from experiments in terms of partial pressure and temperature.

Voutsas and Hatalis carried out experiments to identify the conditions under which a polycrystalline structure of silicon is favored over amorphous silicon. They developed a theoretical model, based on surface diffusion length, to explain the formation of different phases in silicon deposition and to obtain critical conditions characterizing the different structural regimes. Nevertheless, the boundary between amorphous and crystalline regions is defined in terms of growth rate and temperature, as in Bloem. They also use the surface diffusion length to describe grain size.

In view of the interest in and the importance of the crystalline nature of deposited silicon films, it is appropriate to make an attempt to theoretically determine the regions in which each of amorphous, polycrystalline and monocrystalline structure is defined in terms of pertinent deposition conditions. Distinction between polycrystalline and monocrystalline silicon film is quite hampered by extrinsic conditions that can dominate the fate of the

grown film. It is well known for instance, that low temperature silicon epitaxy is dominated by a small amount of water and/or oxygen that leads to the oxide formation at the interface. On the other hand, distinction between crystalline and non-crystalline (amorphous) structure is relatively simpler since extrinsic conditions play only a minor role by the nature of amorphous film deposition, i.e., simple accumulation of adatoms with little migration in the amorphous film formation.

In this communication, an attempt is made to theoretically define regions in which an amorphous film is formed in terms of pertinent deposition conditions, i.e., a "phase diagram" in terms of temperature and partial pressure of source gas.

Probabilities are utilized to arrive at a relationship that defines the boundary for monocrystalline region in terms of the partial pressure of the source gas and the deposition temperature. Also derived is a relationship for the average grain size of polycrystalline film. The results are restricted to the complete or near-complete condensation case of nucleation.

2. Theory

i) Intrinsic phase boundary between amorphous and polycrystalline

Any film deposition from a gas phase is governed by sequential events of adsorption from the gas phase, forming adspecies on the surface, and migration of these adspecies while some of them desorb. The main factor that determines the crystallinity of the grown film is, therefore, the rate of net adsorption relative to the rate of migration. That is, an amorphous film should result if the rate of net adsorption is much larger than the rate of migration. Here, the net rate of adsorption is the rate of adsorption minus the rate of desorption. Therefore, one can write a condition for amorphous film formation as follows:

$$\textit{Net adsorption rate} \gg \textit{migration rate} \qquad (1)$$

If we follow the usual kinetic theory, the condition can be written as follows(Ref. 1):

$$\frac{p}{(2\pi mkT)^{\frac{1}{2}}}(1-\theta)\exp\left(\frac{-E_a}{RT}\right) \gg \nu_o N_a \exp\left(\frac{-E_D}{RT}\right) \qquad (2)$$

where p is the partial pressure of the source gas, θ is coverage which is N_a/N_t, N_a is the surface concentraion of adspecies, k is Boltzmann constant, m is the mass, N_t is the total number of sites, ν_0 is the vibration frequency, and E_a and E_d, respectively, are the activation energies for adsorption and desorption.

it can be written in the following final form:

$$p \geq C' \exp(-\frac{Q}{RT}) \tag{3}$$

ii) Crystallinity of Silicon Film

To develop the basic concept into a relationship, it is necessary to represent the probabilities in terms of specific quantities. One way is to use the expected value of time for the probabilites : the time it takes for an adatom to reach the step ,τ_s, and the time it takes for an adatom to reach an existing stable nucleus, τ_n. When the expected value of τ_s is much larger than that of τ_n, a polycrystalline structure would result, i. e., a monocrystalline structure when $\tau_n > \tau_s$.

According to the basic concept developed so far, the condition for the monocrystalline structure is

$$\frac{\langle \tau \rangle_s}{\langle \tau \rangle_n} < 1 \tag{4}$$

iii) Average Grain Size for Complete Condensation

Let the average grain size be β. Then,

$$\beta^2 \propto \frac{1}{N_s} \tag{5}$$

Using Eqs.(Ref. 4) and rearranging yields

$$\beta = C_2 p^{-n/2} \exp(-\frac{E_d - 2nE_a}{4kT}) \tag{6}$$

It is seen that the average grain size β is inversely proportional to $p^{n/2}$ and dependent on temperature exponentially.

$$\ln \beta = \ln C_2 - \frac{n}{2} \ln p - \frac{E_d - 2nE_a}{4kT} \quad (7)$$

The value of n can be obtained from experimental data at a given temperature by plotting ln β against ln p. The data are those obtained by Voutsas and Hatalis[6] for Si. The slopes indicated in the figure show that n is around 0.9.

3. Results and Discussion

The value of Q obtained from plot is 51 kcal/mol. Their source gas for the silicon deposition is SiH_4. The adspecies for the source gas is SiH_2. The heat of adsorption obtained from a quantum-mechanical calculation by Chernov is 54 kcal/mole. The agreement for the heat of adsorption adds credence to the proposed criterion for the phase boundary between amorphous and polycrystalline region.

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