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ON THE GROWTH FROM THE AMORPHOUS PHASE IN SEMICONDUCTORS

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Résumé - On développe un modèle de croissance d'une phase ordonnée basé sur la diffusion des lacunes thermiques produites à l'interface avec l'amorphe. Il fournit pour Ge et Si la dépendance exacte du taux de croissance pour les couches évaporées et les couches implantes avec la température, l'état de l'orientation cristallin, le dopage, l'ionisation et la nature des ions implantés.

Abstract - A model of growth based on the diffusion of thermally generated vacancies to the interface is developed which provides the exact dependence of the growth rate with temperature, crystalline orientation, doping, ionisation and nature of implanted ions in evaporated as well as implanted layers, for both Ge and Si.

I - Introduction

The aim of this communication is to show that the growth, being an intrinsic property of the material, is related to its fundamental characteristics. Basically, we shall demonstrate that the growth is related to self-diffusion and quenching phenomena in crystals which are directly connected to the formation energy of the intrinsic defect present at thermal equilibrium. This allows us to justify quantitatively the variation of the growth rate with the temperature, the crystalline orientation and various other parameters such as doping, ionization and laser irradiation. In turn, this provides a proof that the thermally induced defects in semiconductors are vacancies and explains how self-diffusion and quenching data are related (1). Finally, we shall see how the difference of growth behaviour between evaporated and implanted layers necessarily implies (2) that implanted layers are not amorphous but disordered (i.e. contain vacancy clusters).

II - The growth in semiconductors

Due to its potential interests, the growth of semiconductors from the solid (amorphous) phase has been extensively studied (for a compilation of the references see ref. 2). However, the way atomic rearrangement is induced at the crystalline-amorphous interface has not been determined and the activation energy Q associated with the growth rate $V_g$ has not been justified. Moreover, the discrepancy between the growth behaviour (see Table I) in evaporated and implanted layers (a variation of Q by a factor of $\sim 2$ in both Ge and Si) has not been explained.

In the next section, we describe a model which justifies quantitatively these activation energies and their difference in evaporated and implanted layers, for both Si and Ge. Then, in section IV, we briefly discuss how such model provides the exact dependence of $V_g$ with the crystalline orientation and explains the variation of $V_g$ with the nature and concentration of the doping (as well as with ionization and laser irradiation), and with the nature of the implanted ions.

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Table I

<table>
<thead>
<tr>
<th></th>
<th>$Q_E$ (eV)</th>
<th>$Q_I$ (eV)</th>
<th>$Q_{SD}$ (eV)</th>
<th>$Q_Q$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>4.6 - 4.9</td>
<td>2.3 - 2.5</td>
<td>4.7 - 5.1</td>
<td>2.5</td>
</tr>
<tr>
<td>Ge</td>
<td>3.0</td>
<td>2.0</td>
<td>3.0</td>
<td>1.7 - 2.1</td>
</tr>
</tbody>
</table>

Activation energies $Q$ (eV) associated with the growth rate in Ge and Si evaporated ($Q_E$) and implanted ($Q_I$) layers and comparison of these energies with activation energies associated with self-diffusion ($Q_{SD}$) and quenching ($Q_Q$). A compilation of the references can be found in ref. 2 for $Q_E$ and $Q_I$ and in ref. 3 for $Q_{SD}$ and $Q_Q$.

III - Model of growth

Examination of Table I shows that, within experimental accuracy, the activation energies $Q_E$ associated with $V_g$ in evaporated layers, for both Ge and Si, is equal to the activation energy associated with self-diffusion. Therefore, self-diffusion is the limiting process of the growth: growth occurs when vacancies created thermally migrate to the interface, thus allowing the jump of an atom from the amorphous to the crystalline phase. The growth rate $V_g$ is then proportional to the probability to form a vacancy times the Boltzmann factor associated with the migration:

$$V_g = \delta v \exp \left( -\frac{E_F}{kT} \right) \exp \left( -\frac{E_m}{kT} \right)$$

where $\delta$, $v$, $E_m$ and $E_F$ are respectively the interatomic distance, the atomic vibrational frequency, the migration and formation of the vacancy (4). Since $E_F + E_m = Q_{SD}$, we have $Q_E = Q_{SD}$. Such model fits the variation of $V_g$ versus temperature using reasonable entropy factors (2).

What about the growth in implanted layers? An implanted layer, originally crystalline or even amorphous, contains necessarily vacancy clusters formed following the cascade of displacements produced by the implanted ions. In that case, vacancies originate from these clusters because, as shown in ref. 1, the formation energy of a vacancy originating from a cluster surface is smaller: $0.5 E_F$. Thus, the activation energy associated with the growth of implanted layer is $Q_I = 0.5 Q_E$ since $E_m$ is very small compared to $E_F$ (vacancies migrate well below room temperature). This situation is similar to the situation encountered in a quench: cooling induces the sursaturation of vacancies and results in vacancy clusters; indeed, as shown in Table I: $Q_I = Q_Q$, the activation energy associated with quenching.

Thus, the model justifies quantitatively $Q_I$ and $Q_E$ for both Ge and Si; the difference between $Q_I$ and $Q_E$ is a result from the fact that implanted layers contain vacancy clusters, i.e. is disordered and not amorphous.

IV - Consequences

The model is able to do more than to provide the exact values of $Q_E$ and $Q_I$ in both Ge and Si. As it is developed elsewhere, it accounts for the dependence of $V_g$ with the various parameters so far studied (a compilation of the corresponding references is in ref. 2), thus providing several other proofs of its validity.
IV.1 - Orientation dependence

According to the model, \( V_g \) is proportional to the distance \( s \) between growth planes and inversely proportional to the density of atoms in these planes. The calculation (2) provides the exact experimental variation of \( V_g \) with the crystalline orientation. Only, for orientation close to the (III) direction, is the calculated rate larger than the experimental one. This is not surprising since, for such orientation, the interface is perturbed by the easy reconstruction between (III) dangling bonds.

IV.2 - Dependence on the nature of the implanted ions

Because migrating vacancies can be trapped by impurities (such as \( O \) to form A centers) or voids (formed by implanted rare gases), it is not surprising that oxygen and other impurities, as well as rare gases, decrease the rate of growth.

IV.3 - Doping dependence

Self-diffusion is dependent on the nature and concentration of the dopant because the migration energy of the vacancy varies strongly with its charge state, function of the Fermi level position. The growth rate varies accordingly. This explains quite readily the enhancement of \( V_g \) under ionization, such as the ones produced by electron or laser irradiation (in this last case it is not possible to predict quantitatively the variation of \( V_g \) because the increase of temperature is not well known).

V - Conclusion

In conclusion, we have demonstrated that the growth in semiconductors is induced by thermally generated vacancies. This simple model provides the exact values of the activation energies associated with the growth rate \( V_g \) in both Ge and Si, for both evaporated and implanted layers and is in complete agreement with self-diffusion and quenching data. It explains the crystalline orientation dependence of \( V_g \), its variation with doping, ionization and nature of the implanted ions. Finally, it shows that implanted layers are not amorphous but contain vacancy clusters.

References

1. BOURGOIN J.C., unpublished.
4. It is shown in ref. 1 that vacancies are the thermally generated defects because self-diffusion and quenching data cannot be reconciled if the defects are interstitials.