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Surfactant effect on the surface diffusion length in epitaxial growth

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It is shown that Te and Pb, which segregate at the surface during the epitaxial growth of GaAs, respectively, decrease and increase the surface diffusion length. This indicates that under the generic term "surfactant," there are two types of surface segregating species which have opposite effects on the surface diffusion. It is suggested that the key parameter which imposes the surfactant-induced modification of epitaxial growth kinetics is the reactivity of a given pair of surfactant and growing material. Following this approach, it is concluded that surfactants occupying interstitial surface sites (nonreacting surfactants) increase the surface diffusion length whereas surfactants in substitutional sites (reacting surfactants) decrease it.

It has been recently demonstrated that the use of surfactants can improve the epitaxial growth of strained materials such as Ge on Si (Refs. 1 and 2) or (In,Ga)As (Refs. 3 and 4) on GaAs. The concept underlying the term "surfactant" comes from the thermodynamical foundation of epitaxial growth.[5,6] Strictly speaking, a surfactant is simply a species which when added to a given surface lowers its surface free energy. When used, the energetic balance of surface and interface free energies of the materials involved in the growth is changed, allowing possible control of the growth mode. This was indeed the original idea underlying the first experimental work in this area.[1] However, it was soon recognized that the important effect of a surfactant is the modification of the epitaxial growth kinetics.[1,7] Even if there is now a consensus on this point, as well as on the fact that a surfactant should segregate to be efficient, the situation is still confused, at least at first sight, as to how it changes the incorporation kinetics of the growing material. Convincing experimental results have been reported which prove that a surfactant *decreases*[4,7] or conversely *increases*[8-10] the mean surface diffusion length of incorporating atoms, which in fact controls the growth. This contradiction is only apparent and comes mainly from the fact that the term "surfactant" is mainly used to specify a segregating species which improves the growth of the material under consideration. Considering in more detail the published data, it appears that surfactant species which are found to be efficient in improving homoepitaxial growth are useless for heteroepitaxial growth of strained materials.[11,12] One easily understands that to improve homoepitaxial growth, a surfactant should increase the surface diffusion length, while, on the other hand, the opposite effect is desired in the case of lattice mismatched epitaxial growth, in order to avoid the formation of three-dimensional (3D) islands which correspond to the equilibrium situation. The question which clearly remains now is how to predict the effect of a given segregating impurity on the growth of a particular material system.

The aim of the present paper is to extract from the comparison of the effect of different segregating species (namely, Te and Pb), on the same growth material (GaAs), a simple rule to help in choosing a surfactant adequate for the desired purpose.

Experiments have been carried out in a molecular-beam-epitaxy system equipped with a standard *in situ* reflection high-energy electron diffraction (RHEED) facility and coupled to an analysis chamber where x-ray photoelectron spectroscopy (XPS) can be performed. After the growth of a GaAs buffer layer (~ 1 μm) at 580 °C on a GaAs(001) substrate, the sample was exposed to a Te or Pb flux at ~ 400 °C. Then the temperature was increased in order to obtain a 3×1 and a 1×3 reconstructed GaAs(001) surface for Te and Pb, respectively. These reconstructions appeared at ~ 580 °C for Te and ~ 420 °C for Pb and correspond to a surface coverage (estimated from XPS measurements) of 0.6 monolayer (ML) and 0.5 ML, respectively, which agree well with previously reported values.[13,14] The surface segregation of these two different species during the growth was checked by XPS. Growth rates were precisely measured by using RHEED specular beam intensity oscillations. The RHEED pattern was recorded using a high-sensitivity charge-coupled device camera and a video system. A precise determination of diffraction intensity was performed by image acquisition and dedicated analysis software.

It has been already reported that Te acts as a surfactant for highly strained material growth such as $In_xGa_{1-x}As/GaAs$ (Refs. 3 and 4) or Ge/Si.[15] As 3D island formation is avoided, the conclusion was that Te reduces the surface diffusion length (SDL). A more straightforward proof is however to compare, for a fixed set of growth parameters, the temperature for which the growth mode with and without Te changes from 2D nucleation to step propagation. This transition is linked to the disappearance of RHEED intensity oscillations and can be easily attained by using vicinal surfaces.[16] For this purpose we have performed GaAs growth as a function of temperature with and without the Te surfactant layer on 5° misoriented surface toward the (111)Ga plane (which corresponds to a mean terrace length of 32 Å). The growth rate was fixed at 1 ML/s with a flux of As_4 corresponding to a maximum As incorporation rate of 2.5 ML/s. The variation of the specular beam intensity

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as a function of the growth temperature is reported in Fig. 1. The transition temperature where RHEED oscillation disappears is found to be around 580 °C for standard growth and 600 °C for Te mediated growth. The fact that the growth by step propagation is more rapidly obtained in standard growth when increasing the temperature clearly indicates that the SDL is, for a given temperature, larger than in the case of Te mediated growth.

While for the growth of $In_xGa_{1-x}As$ ($x > 0.25$) on GaAs the 2D-3D growth mode transition is delayed when using Te as surfactant and the critical thickness is significantly increased,[17] no such improvements are observed with Pb. Actually the critical thickness is even lower than for the standard growth. This seems to indicate that in fact Pb increases the SDL. Unfortunately, it is not easy to verify this hypothesis by using the same approach as above (i.e., the determination of the critical temperature of the 2D nucleation-step propagation transition) because Pb is desorbed from the surface for temperatures as low as 450 °C. However, in the low-temperature range another phenomenon can be used to evaluate the effect of surfactant species on the SDL. For low enough temperature, there is no long-range atomic diffusion, and a surface roughness develops during growth which may be easily detected in RHEED. In order to investigate the influence of the Pb segregating layer on this kinetic roughening, we have compared the growth behavior of GaAs at low temperature (400 °C) with and without Pb. The results deduced from RHEED analysis are reported in Figs. 2 and 3. In Fig. 2(a), corresponding to the standard growth, it may be noted that the mean specular beam intensity during the growth is higher than the static level before growth. This is well known to occur because the static surface reconstruction at this temperature is $c(4\times4)$ while during growth it becomes 2×4.[18] The important point is that growth oscillations are very weak and rapidly damped, indicating that at this temperature the SDL becomes too low to sustain the pure 2D layer-by-layer growth. This results in a growth front roughening evidenced by the intensity reinforcement of the 3D Bragg diffraction feature on the RHEED pattern. This can be seen in Fig. 3(a) where the RHEED profile intensity of the 00 streak is displayed as a function of the growth time (the specular and Bragg positions are labeled *S* and *B*, respectively): the Bragg intensity increases rapidly when the growth starts. The SDL is not enough to allow an adatom impinging on the top of a 2D nucleus to migrate to the step edge and consequently the growth front becomes rougher. When the growth of GaAs is performed on the surface which has been previously exposed to a Pb flux [Figs. 2(b) and 3(b)], no such growth front roughening occurs and the variation of the specular beam intensity is similar to the one observed at

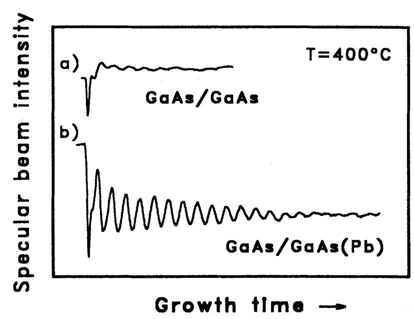

FIG. 2. RHEED specular beam intensity variation as a function of time recorded during the growth of GaAs at 400 °C on GaAs(001): (a) standard growth conditions and (b) Pb mediated growth.

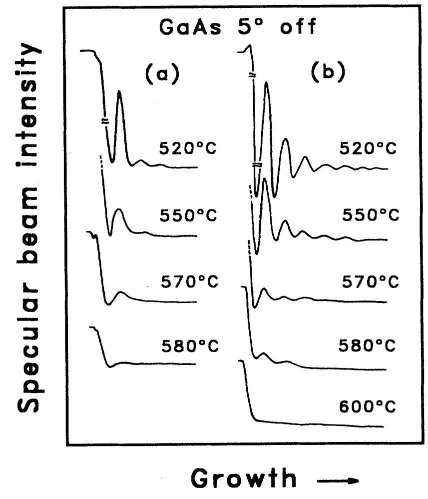

FIG. 1. RHEED specular beam intensity behavior during the growth of GaAs on a 5° misoriented surface (mean terrace length 32 Å) toward (111)Ga plane (e^- beam along [110]) as a function of the growth temperature: (a) standard growth conditions and (b) Te mediated growth.

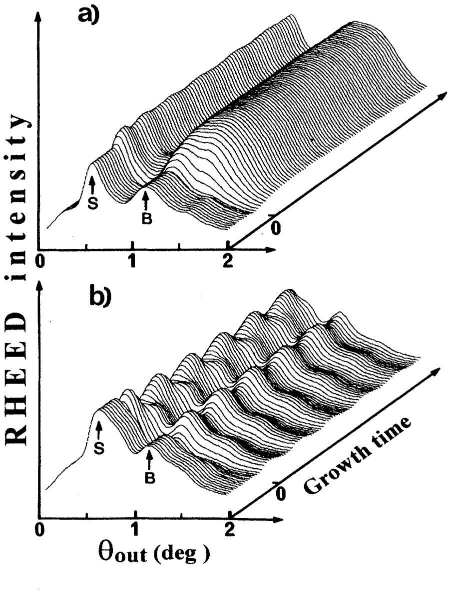

FIG. 3. 3D analysis of the temporal evolution of the 00 RHEED streak intensity during the growth of GaAs at 400 °C on GaAs(001): (a) standard growth conditions and (b) Pb mediated growth. The specular beam and 3D-Bragg intensities are labeled *S* and *B*, respectively.

standard growth temperature (580 °C) [it is worth noting that, as usually observed for standard growth temperature, there is a clear phase opposition between S and B (Ref. 19)]. We therefore conclude that Pb enhances the surface diffusion length. At this point it is important to mention that the same conclusion has been recently drawn for the effect of Sn, also a column-IV element, at the growing surface of Si (Refs. 9 and 10) as well as of GaAs and $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$.[20]

Considering the present experimental results and those previously reported, it clearly appears that there are two families of so-called surfactants. One results in an increase in the SDL and is effective in improving homoepitaxial growth; the other decreases the SDL and is therefore suitable for the growth of highly strained materials for which the main objective is to avoid the formation of 3D islands. Keeping the example of IV and III-V semiconductors, which includes most of the published work in the field, we can classify the different segregating species experimented up to now as follows: column-III and column-IV elements, such as Ga, Sn, and Pb, belong to the first family while column-V (As, Sb) and column-VI (Te) belong to the second. In order to understand, at least qualitatively, the opposite behavior of these different surfactant species, let us now consider the models which have been previously proposed in two typical cases. Enhancement of the SDL by the presence of Sn at the growing GaAs surface is explained by Petrich, Dabiran, and Cohen[20] by considering that Sn is only slightly bonded to the semiconductor surface and located in interstitial-like sites as schematically shown in Fig. 4(a)(i), where for sake of simplicity the growing species is group-IV semiconductor (SC) type. This hypothesis is strengthened by the fact that van der Veen *et al.*[14] have previously concluded from synchrotron photoemission spectroscopy that there is no significant chemical interaction between Pb and GaAs. We suggest that this type of surfactant forms a surfactant SC complex at the surface which, even though weak, is sufficient to decrease for some extent the SC-SC bond strength. This in turn reduces the energy barrier for hopping of the SC atoms at the surface in their way to be incorporated. As a consequence the SDL is increased. Finally, the surfactant follows the growth front rather than being incorporated in the semiconductor [Fig. 4(a)(ii)] because it is more easily complexed at the surface, where dangling bonds are present and where relaxation of the induced strain is easier. The prototypical case of surfactant action of the second type is As on Si or Ge. It has been clearly demonstrated[7] that As significantly reduces the SDL following a mechanism which is summarized in Fig. 4(b). Here the surfactant forms strong bonds with the semiconductor [substitutional sites, Fig. 4(b)(i)]. The segregating process imposes an exchange reaction between adatoms of the growing layer and the surfactant, resulting into subsurface incorporation [Figs. 4(b)(ii) and 4(b)(iii)]. To migrate, atoms have thus to break their existing bonds (including those with the surfactant species) and this leads to a higher barrier for hopping. The net result is that the SDL is reduced.

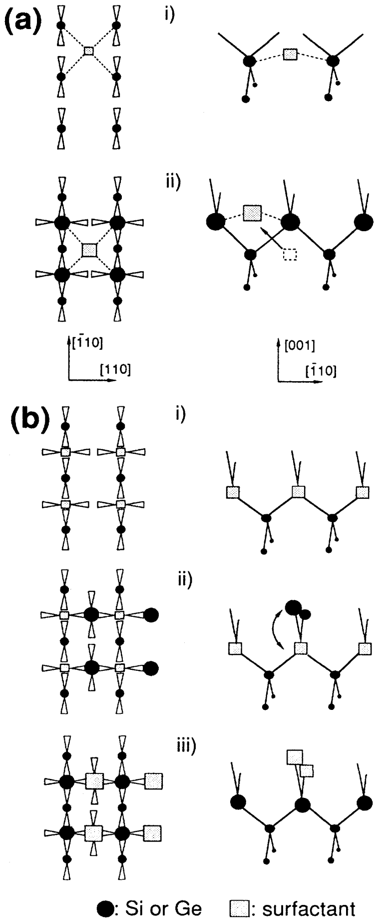

FIG. 4. Schematic representation of atomic mechanisms which differentiate the two different types of surfactants: (a) nonreactive surfactant increasing the surface diffusion and (b) reactive surfactant decreasing the surface diffusion.

The two mechanisms described above lead us to suggest the separation of segregating species termed as surfactants into nonreactive surfactants occupying interstitial surface sites, which result in the increase of the surface diffusion length, and reactive surfactants, in substitutional sites, which have the opposite effect. This may be a guideline for choosing a surfactant suitable for a given purpose. If it is desirable to smooth the growth front in case of homoepitaxial growth, then a nonreactive surfactant should be chosen. On the other hand, when the strain induced 2D-3D growth mode transition should be avoided in lattice-mismatched epitaxial growth, a reactive species must be preferred. We think that taking into account the reactivity of a given couple of segregating species and growing material is essential to correctly predict the resulting effect on the growth kinetics. As a matter of fact, while Sb has been found to decrease the surface diffusion length for Ge/Si growth,[2,12] it has the opposite effect for the homoepitaxial growth of Ag.[21] In the first case Sb is reacting whereas in the second it is not. However, the crude categorization we propose should be somewhat refined in the light of the results very recently reported by Falta *et al.*[22] Indeed these authors have observed that Ga on Si(111) behaves differently depending on the surface coverage. While at first sight Ga may be considered for Si as a nonreactive surfactant, at high coverage (1 ML) and low temperature it *decreases* the surface diffusion length.[22] In fact it has been shown that the (6.3×6.3) surface reconstruction observed in these conditions corresponds to Ga in substitutional surface sites,[23] as expected for a *reactive* surfactant. This reconstruction is however metastable and is replaced above 500 °C by a classical $(\sqrt{3}\times\sqrt{3})$ (surface coverage $\sim\frac{1}{3}$ ML) (Ref. 22) for which Ga atoms occupy interstitial sites,[23] the usual bonding situation of a nonreactive surfactant as described above. Indeed, Ge islanding growth on Si(111) is observed at standard growth temperature (> 500 °C), even if a Ga flux is continuously supplied.[22] These recent results indicate that the *a priori* distinction between potential surfactant species may be not so simple as suggested above, even if our crude categorization can be a useful guideline at least for usual (i.e., "high" temperature) growth conditions. It is clear that a more strict criterion to predict the resulting effect of a given segregating species on the surface diffusion length is the actual bonding configuration at the surface.

In summary, it is shown that Te and Pb, which segregate at the surface during the epitaxial growth of GaAs, have opposite effects on the growth kinetics. While the surface diffusion length is reduced by the presence of Te at the growth front, it is enhanced when Pb is the segregating species. These experimental results, as well as those previously published, lead to the conclusion that there are two types of surfactants. It is suggested that the difference in their resulting effect is linked to their degree of interaction with the growing material: reacting surfactants occupying substitutional surface sites decrease the surface diffusion length while nonreacting surfactants, in interstitial sites, increase it. This can serve as a guide to choose among various segregating species those which can be effective in improving epitaxial growth of a given material system.

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