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Stress induced surface melting during the growth of the Ge wetting layer on Si(0 0 1) and Si(1 1 1)

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Abstract

We compute the isotropic stress for a Ge film deposited on Si(0 0 1) and Si(1 1 1) at $T = 870$ K. By direct comparison with experimental phase diagrams measured for bulk Ge we deduce that Ge melts—at least partially—when deposited on Si surfaces at this temperature, due to the high heteroepitaxial stress (in the range 1–10 GPa), which has also been reported in experimental studies. Surface melting (complete or incomplete) induced by heteroepitaxial stress is consistent with a recent theoretical model proposed in the literature, and may account, at least in part, for the large values of Ge/Si intermixing reported in other studies. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the last few years, several papers have dealt with the crucial aspect of intermixing of different atomic species in the formation of semiconductor quantum dots (QDs) during heteroepitaxial growth [1,2], and in particular, a lot of debate arose around the true composition of Ge QDs grown on Si substrates. However, most of these studies are purely experimental reports and they do not deal with the physical origin of the intermixing phenomenon; furthermore, very few experimental techniques are able to give *direct quantitative* results on interdiffusion: for example Auger spectroscopy and X-ray photoelectron spectroscopy

(XPS) are only capable of giving qualitative information. X-ray absorption fine structure (XAFS), which was employed to study this system using synchrotron radiation at the Ge K-edge by Boscherini et al. and Rosei et al. [1], is well suited for studying the average composition of an alloy, but is not sensitive to local composition gradients or inhomogeneities; moreover, it is not intrinsically surface sensitive, and it therefore cannot give direct information on the intermixing in the QDs. The most accurate technique for this purpose is, notably, medium energy ion scattering (MEIS), but it is severely limited by the fact that it can only probe relatively thin films. It is therefore of fundamental importance to address and clarify the theoretical description of the alloying process in order to find ways to control (in the sense of reducing, or enhancing) the intermixing itself. This is particularly true for Ge/Si, which so far has only been marginally treated

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and where new technological applications may require either a simple graded succession of Ge/Si layers [3], or islands rich in Ge content. Even from a fundamental point of view, the fact that there is intermixing between the two species means that the growth mode cannot be considered a classical Stranski–Krastanov type, but a *modified* one [1].

So far, theoretical description of this phenomenon has been gained by Monte Carlo simulations at equilibrium [4], or by analysing the role of compositional stresses in determining the stability of alloy film growth [5].

In semiconductor heteroepitaxy, there are basically four possible mechanisms for strain relief: (a) island nucleation and evolution (shape transition and faceting); (b) formation of dislocations; (c) intermixing and alloying; (d) formation of trenches around the islands. In most cases, a combination of these four mechanisms takes place; however, it must be emphasized that for the development of applications the formation of misfit dislocations and the occurrence of intermixing can be highly undesired features.

In recent works Bottomley [6,7] proposed new theoretical insight on the formation of semiconductor quantum dots, with particular interest in the phenomenon of intermixing. The main innovative idea is the following: it is suggested that the large heteroepitaxial stress present on semiconductor surfaces during heteroepitaxial growth (in particular for InAs on GaAs(0 0 1); the case of Ge on Si(0 0 1) is only briefly discussed) causes InAs to melt when deposited on GaAs(0 0 1) at about 770 K. This pressure induced surface melting naturally leads to mixing with the substrate in order to obtain a local minimum of the Gibbs free energy of the liquid phase. Bottomley had previously shown [6] that the correct thermodynamic function of state, which is minimized for a stressed material, is in fact the Gibbs free energy.

This is a radical but relatively simple way of accounting for intermixing, through the well known thermodynamic phenomenon of *pressure-induced* melting: the formation of a liquid phase of the deposited material would facilitate mass transport, leading to quantum dot formation. The melting temperature of bulk Ge is known to be $T_M = 1210$ K, which is much higher than the normal temperatures used for heteroepitaxial growth (normally in the range 675–875 K); however, bulk Ge undergoes a high temperature phase

transition (similar to the solid–liquid transition) already at $T_c = 1040$ K [8], with static disordering involving only a few surface layers, and incomplete surface melting [9]. It is therefore not unreasonable to envisage an order to disorder phase transition at a *lower* temperature in the presence of high pressures, especially when dealing with an extremely thin film of material, like in the present case of growth of QDs.

First of all, it should be pointed out that the bulk interdiffusion coefficient of Ge in Si has been estimated [10] to have an activation energy of 3.93 eV, which would lead to an extremely slow intermixing rate in the *bulk*. At first thought it is therefore quite surprising to find such a high degree of intermixing as the ones which have been previously reported (from 25% to up to 50%, depending on the total amount deposited, on the growth temperature, and on the type of growth, for example, molecular beam epitaxy (MBE) or chemical vapor deposition (CVD)), especially in studies where relatively low temperatures were used for growth [1], even though in these cases we are concerned with interdiffusion at the interface, not in the bulk.

When applied to the Ge/Si(0 0 1) system for a growth temperature of about 970 K, Bottomley's calculations again predict a liquid phase [6,7], and in the limit of equilibrium thermodynamics the molten Ge should mix with the Si substrate to yield an alloy of approximate composition $\text{Si}_{0.5}\text{Ge}_{0.5}$. This prediction is consistent with the results reported by Rosei et al. [1] for the wetting layer of Ge on Si(1 1 1), but at a much lower growth temperature (about 770 K).

In principle, this result—in spite of the inconsistency on the temperature—is not so surprising after all: in fact if one writes down the expression of the thermodynamic force acting on a Si and on a Ge atom at opposite sides of the Ge/Si interface, one would find [11] that they have opposite signs, meaning that Si wants to diffuse into the Ge layers, and vice versa.

Clearly hydrostatic pressure has the effect of reducing the melting point of both Ge and Si; in the early 1960s the phase diagram for several semiconductor systems were studied in detail [12,13]. In the case of Ge, from these diagrams we infer that a pressure of approximately 10 GPa is needed to melt bulk Ge at a temperature of about 825 K. We would like to point out here that recent experimental works [14] measure an incremental compressive film stress in the range of

–2.8 to –5.8 GPa (in the temperature range 820–970 K) for Ge grown on Si(0 0 1) and up to $-7 \pm 10\%$ GPa (constant in the temperature range 700–1000 K) for Ge on Si(1 1 1). Previously, a compressive stress of –5.65 GPa (at $T = 770$ K) was observed in the wetting layer by Shell-Sorokin and Tromp [15].

In order to contribute to this point, we used classical molecular dynamic simulations to estimate the hydrostatic stress in two different series of samples: a continuous epitaxial Ge film deposited on the Si(0 0 1) and Si(1 1 1) surfaces. The atomic interactions have been computed according to the Tersoff potential [16], which allows for a good description of the elastic properties of Ge/Si compounds; the stress tensor was computed, according to the formulation proposed in [17], on the average atomic positions at $T = 875$ K for orthorhombic simulation cells containing at least 10,000 atoms; in this context, a negative value of the stress tensor means compressive stress. A thorough description of the methods used for the calculations and the molecular dynamics relaxations has been reported elsewhere [18,19].

Table 1

Computed values of isotropic stress for Ge deposited on Si surfaces at 875 K

	Isotropic stress (GPa)	Isotropic stress (kbar)
Ge on Si(1 1 1)	-7.5 ± 1.5	-75 ± 15
Ge on Si(0 0 1)	-3.0 ± 0.6	-30 ± 6

Remarkably, we find an isotropic stress in the range of –6 to –9 GPa for Ge on Si(1 1 1) and about –3 GPa for Ge grown on Si(0 0 1). Our results are summarized in Table 1, where they are also reported in kbar for a simpler comparison with the graph from [12]; for direct comparison, we also report the experimental results from [14,15] in Table 2, from which it can be seen that our numerical calculations are consistent with the experimental values previously reported.

In Fig. 1 we report the phase diagram adapted from [12], on which we superimposed the experimental points from [14,15] and our calculated data points. By comparing these results we infer that this “pressure” is almost sufficient to melt (at least partially) the

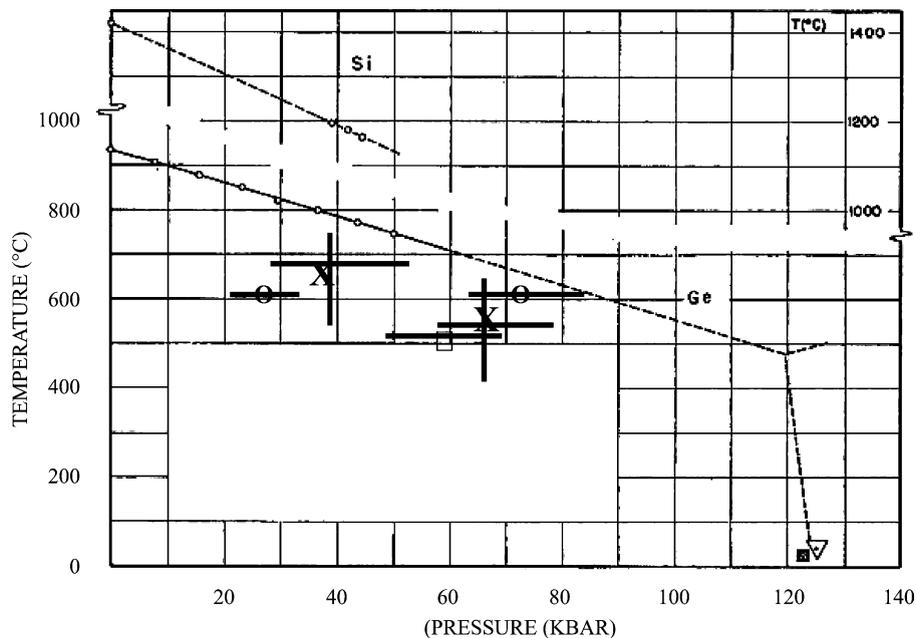


Fig. 1. Melting phase diagram for bulk Si and Ge, and proposed phase relations for Ge, adapted from Ref. [12]. Superimposed as circles (○) with error bars are our simulated data points; experimental points marked with a capital X [14] and marked with a □ symbol [15] are also superimposed together with their error bars.

Table 2
Compressive stress from previous experimental studies

	Temperature range (K)	Measured compressive stress (GPa)	
		From [15]	From [14]
Ge on Si(0 0 1)		$-5.65 \pm 10\%$	–
Ge on Si(0 0 1)	820–970	–	$-4.3 \pm 1.5\%$
Ge on Si(1 1 1)	700–1000	–	$-7 \pm 10\%$

deposited Ge at this temperature. Moreover, it must be emphasized that the phase diagram for Ge reported in [12] has been measured for the bulk material, whereas in this case we are dealing with a thin film in the best case; it is very likely that the melting temperature further reduces when the system is made up of a few layers only.

It must be noted that here we are not in the presence of hydrostatic pressure, but of planar stress. A compressive biaxial stress, as well as a hydrostatic one, induces a reduction of the average atomic volume. Therefore the liquid phase, which has a higher density, should be favored and a partial melting of the Ge film can occur at the higher pressure/temperature conditions, especially if deposited on a Si(1 1 1) substrate where the induced stress is stronger. Moreover, the elastic energy stored in the epilayer should favor atomic mobility; adatoms will have an excess energy which will enable them to overcome diffusion barriers more easily [11].

Therefore, the intuition that the compressed Ge should become more mobile (even without actually melting) is qualitatively well justified. This means that the process of atomic exchange (which in principle is too slow to be significant at the relatively low temperatures used for growth) can be strongly accelerated in the Ge layers which are compressed, but not into the Si layers which are expanded.

2. Conclusions

In conclusion, with the present contribution we have discussed several aspects of the phenomenon of alloying at the Ge/Si interface, reinforcing the idea that the large values of intermixing reported experimentally are caused by surface melting (at least partial) of Ge when grown on Si surfaces, in addition to other causes such as surface diffusion.

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