Molecular-beam epitaxy of Ge on GaAs(001) and Si capping

I. Goldfarb
Department of Solid Mechanics, Materials, and Systems, The Fleischman Faculty of Engineering, Tel Aviv University, Tel Aviv 69978, Ramat Aviv, Israel

J. L. Azar, A. Grisaru, E. Grunbaum, and M. Nathan
Department of Physical Electronics, The Fleischman Faculty of Engineering, Tel Aviv University, Tel Aviv 69978, Ramat Aviv, Israel

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Epitaxial quality of Ge layers on GaAs(001), as well as the quality of the Si capping layers, were investigated in situ by reflection high-energy electron diffraction during growth and, subsequently, by scanning electron and scanning probe microscopies. Ge was grown on the (1×1)-GaAs(001) surface prepared by oxide desorption at 580 °C in an As-free ultrahigh vacuum; its morphology, varying from reasonably flat layers with only atomic scale roughness to relatively large three-dimensional asperities, was found to crucially depend on the GaAs surface quality and growth temperature. The data presented in this work also account for the apparent discrepancies between various groups regarding the Ge/GaAs reconstruction; our detailed analysis proves that, at least under the experimental conditions described herein, it is a mixture of (1×2) and (2×1), rather than a (2×2) or c(2×2). Smooth Si growth was mainly impeded by a large lattice mismatch with the underlying Ge, initially replicating the morphology of the Ge layer and eventually forming discrete three-dimensional islands and continuous undulations. The study shows that flat epitaxial Si capping of GaAs should be possible by employing graded silicon–germanium buffers. © 2003 American Institute of Physics. [DOI: 10.1063/1.1542656]

I. INTRODUCTION

Heteroepitaxial growth of group-IV elemental semiconductors on III–IV compound semiconductors stimulates both basic and applied research. The basic interest stems from the fundamental importance of the interface atomic structure between two dissimilar materials, especially between lattice-mismatched and/or nonpolar group-IV and polar III–IV atomic planes, and its effect on the electronic characteristics of such heterostructures, in particular energy band offsets across the interface.1–5 One of the most important applications of group-IV on III–V compound (IV/III–V) heterostructures, is in the area of metal/oxide/semiconductor field-effect transistor technology, that has been suffering from the high density of interface states and, thus, Fermi-level pinning. It has been long known that growth of pseudomorphic Si layers on GaAs, as a preliminary step to the formation of SiO$_2$/GaAs, is helpful in reducing this sort of problem,6–8 seemingly due to the formation of good quality SiO$_2$/Si interfaces.9 The concept of combining the beneficial properties of GaAs, e.g., high speed and high power, on the one hand, and the ease of forming the Si oxide on the other hand, is impeded by the ~4% Si/GaAs lattice mismatch and corresponding strain-limited layer thickness and perfection. The latter problem can be minimized by using graded Ge$_{1-x}$Si$_x$ buffers between Si and GaAs, where x ultimately varies from 0 (pure Ge) to 1 (pure Si), which is similar but reverse to the Si$_{1-y}$Ge$_y$ buffers between Ge and Si.10 Ge on GaAs is sufficiently interesting by itself, with Ge/GaAs being a model system due to a less than 0.1% lattice mismatch, and the possibility to match nonpolar Ge atomic planes with nonpolar, e.g., (110), or polar, e.g., (100) and (111), GaAs surfaces. Tunable band gap properties of such heterojunctions can be used in device design. The high hole mobility of Ge has a large potential for high-speed heterobipolar Ge/GaAs transistors,11 strong absorption in the 1.0–1.5 μm range explains why the Ge–GaAs system is widely used in solar cells,12 and transparency in the midinfrared 3–10 μm range makes it a good waveguide in GaAs-based integrated electro-optics.13–15

In view of such promising features of Si/GaAs and Ge/GaAs heterostructures, and the strong interrelation between the growth microstructures and their physical properties, there are surprisingly few publications concerned with the detailed analysis of their respective growth characteristics.16–22 Bratina et al.18 have used molecular-beam epitaxy to grow Si on GaAs(001)-(2×4) (prepared by oxide desorption at 580 °C at As$_4$ overpressure), and found that a (3×1)-reconstructed Si layer grew two-dimensionally up to 3–4 monolayers, after which initiation of three-dimensional (3D) growth was detected in reflection high-energy electron diffraction (RHEED).18 The latter is not surprising in view of the high Si/GaAs mismatch. In fact, the mismatch is similar to that of Ge/Si, and even the resulting Stranski–Kranstanow (S–K) wetting layer is, therefore, of a similar thickness. One of the most recent papers by Wang et al.19 accounts for the observed reconstructions at submonolayer Si/GaAs(001) coverages, using scanning tunneling microscopy (STM);19 however, it does not deal with...
thicker Si layers. More work can be found in literature on Ge/GaAs(001), c.f. Refs. 20–22, using a wider variety of experimental methods, such as RHEED, transmission electron microscopy,16,17 STM,22 low-energy electron diffraction,20 high-resolution x-ray diffraction,21 etc. Again, most of these describe only the initial stages of epitaxy, and all of them use As-stabilized either (2×4), c(4×4), or c(2×8) GaAs(001) surfaces for growth. The preparation of such surfaces requires either GaAs homoepitaxy or, at least oxide desorption in the presence of As₂ or As₄ flux, which significantly complicates the process.

The goals of this work were three fold: (i) to investigate the effect of layers thickness on the epitaxial quality of the overgrowth, (ii) to introduce a Ge buffer layer between the Si epilayer and the GaAs substrate, and (iii) to explore growth on a GaAs(001)-(1×1) surface resulting from a simple preparation, avoiding the use of As.

II. EXPERIMENT

Epiready GaAs(001) wafers from Wafer Technology Ltd. were cleaned ex vacuo with an ultrapure nitrogen gas and introduced into a UHV Varian VT-422 system (base pressure 10⁻⁷ Pa), equipped with two magnetically focused electron guns for evaporation from water-cooled copper crucibles and a RHEED gun (Oxford Applied Research) for monitoring. The GaAs samples were then gradually heated in the UHV to 580 °C, where oxide desorption takes place, with continuous RHEED monitoring of the evolving surface, until the appearance of a reasonably ordered (1×1) streak pattern (see Fig. 1).

At this point, Ge and/or Si evaporation onto so-prepared substrates was initiated. The thickness of the growing layer was monitored by a Inficon quartz thickness monitor (for each evaporant), whereas the degree of crystalline perfection and morphological evolution was determined by RHEED. In the particular set of experiments described here, Ge layers of varying thicknesses were deposited first at several temperatures, and then capped by Si layers with similarly varying thicknesses and temperatures, in order to optimize the conditions for a maximally smooth growth with minimal interdiffusion. To change the temperature, the growth was stopped and then renewed after the new temperature was established. For example, a typical Si/Ge/GaAs sequence consisted of Ge growth immediately following oxide desorption from the GaAs surface at 580 °C, growth interruption, temperature lowering to 480 °C, and initiation of the Si growth. Due to technical reasons, it was difficult to maintain continuous operation of the evaporation sources at less than 0.8 nm/s (on average) rate, which explains the relatively high deposition rates employed in this study. Such layered samples were then taken out of the vacuum and systematically analyzed by atomic force (AFM) and scanning electron microscopy (SEM).

III. RESULTS

A. Ge growth on GaAs(001)-(1×1) surface

GaAs substrate surface quality is paramount to any successful epitaxy, hence, the importance of the surface preparation procedure. For example, as explained by Neave et al.,17 the excess As on the (4×4) surface makes it inferior for Ge growth when compared with the intrinsic (2×4)-reconstructed GaAs surface, where Ge can bond directly to the GaAs lattice, resulting in a (2×2),17 or (2×1) reconstruction according to Wang et al.22 The lack of a sufficient amount of As atoms on the surface, on the other hand, may lead to a Ge—Ga bonding, creating a (1×2) superstructure.22

Figure 1 shows the evolution of GaAs(001) surface with anneal. It is evident from the three RHEED azimuths that, up to about 500 °C, the surface exhibits diffused intensity distribution in the shape of an amorphous halo, characteristic of a disordered substance [Figs. 1(a)–1(c)]. Above 500 °C, the oxide begins to desorb, and initial stages of atomic ordering can be observed via some visible, even if diffused, streaking [Figs. 1(d)–1(f)]. The process is completed at 580 °C, where the streak structure of the RHEED patterns indicates reasonable surface ordering [Figs. 1(g)–1(h)], in a bulklike (1×1) termination. The term “reasonable” is used here to describe a two-dimensional (2D) layer with, however, a certain degree of disorder or roughening on the atomic scale. An ultimately ordered monocrystalline layer would have produced only spots lying on the Laue circles, rather than streaks resulting from the intersections of the Ewald sphere with finite-size reciprocal lattice rods, due to deviations from the ideally perfect surface, e.g., small size of coherently scattering domains.23 Yet, such a surface is a good enough substrate [Figs. 2(a)–2(c)] for a similar 2D Ge growth, as shown in Figs. 2(e)–2(l), even with a lesser level of atomic-scale roughening (smaller degree of spotiness along the streaks). In addition to understanding the Ge epilayer morphology, these RHEED patterns shed light on the controversy related to the reconstruction of Ge/GaAs(001). Even after 10 s of Ge deposition (about 80 Å) at 580 °C, faint half-order streaks in both [110] and [110] azimuths were observed, whereas no fractional order streaks were detected in the [100] azimuth [see Figs. 2(d)–2(f)]. This indicates the beginning of the well-known mixed (1×2) and (2×1) reconstruction, which is inherent to Si(001) and Ge(001) surfaces,23 and gets stronger.
after 60 and 120 s of deposition [500 Å in Figs. 2(g)–2(i) and 1000 Å in Figs. 2(j)–2(l), respectively]. Such patterns unequivocally identify mixed (1×2) and (2×1) reconstructions; they contradict the previously proposed (2×2),16 c(2×2),17 and single-domain (1×2) or (2×1) reconstructions,20,22 because in (2×2) half-order streaks should have appeared in a [100] azimuth as well, in c(2×2) half-order streaks should have appeared only in the [100] azimuth, and in single-domain (1×2) or (2×1) half-order streaks are only expected in either [110] or [110] azimuth, respectively.

Several factors may account for the aforementioned discrepancy. To begin with, the GaAs(001)-(1×1) substrate termination in this study is different from the common (2×4), c(4×4), or c(2×8)-reconstructed GaAs(001) surfaces.20–22 This may lead to a different bonding of the Ge atoms to the substrate, and may result in different energetics and, hence, in a different reconstruction. Misinterpretation of experimental data can account for the discrepancy in other cases, e.g., a minimum of three reciprocal lattice directions must be sampled to distinguish between different reconstructions, and, therefore, a single or even two RHEED azimuths may lead to inaccurate identification. Finally, using only indirect techniques, such as all kinds of spectroscopy and diffraction without direct surface imaging, may create the wrong impression. For example, Figs. 2(m)–2(o) show three RHEED azimuths from the almost pure Si (Si₈₀Ge₂₀) layer, capping the Ge/GaAs(001) epilayer described in the previous paragraph. After 80 s of deposition, the cap exhibits a (1×1) reconstruction [Figs. 2(m)–2(o)]. However, after 120 s (about 1000 Å thickness), it appears at first sight that the reconstruction changes to a single-domain (2×1) [Figs. 2(p)–2(r)], because half-order streaks are only observed at the [110] azimuth [Fig. 2(p)]. A closer look reveals that the spotiness, or the degree of intensity modulation along the streaks, is substantially higher along the [110] azimuth [Fig. 2(r)] than along the [110] azimuth [Fig. 2(p)], indicating some sort of preferentially oriented 3D structure. This trend is further amplified in the Si-cap layer [compare Figs. 2(s) and 2(u)]. An SEM micrograph of the cap surface, shown in Fig. 3, indeed displays surface undulations, or ripples, aligned preferentially along one of two (110) crystallographic directions. It becomes immediately apparent that when the RHEED beam is incident parallel to the ripples, it will “see” both the 3D ripples and the (1×2) and (2×1)-reconstructed 2D surface between them. However, in the perpendicular direction, only a 3D transmission pattern will result, in accord with RHEED characteristics in Figs. 2(s)–2(u). Thus, evidently, Si, Si₈₀Ge₂₀, and Ge on GaAs(001) reconstruct in the familiar intrinsic double-domain (1×2) and (2×1) way. However, preferential orientation of the strain-induced surface ripples may create a misleading impression of a single-domain (2×1) superstructure.

The most pivotal factor affecting the epitaxial growth of Ge on GaAs, at least in this study, was found to be the degree of crystalline perfection of the initial GaAs(001)-(1×1) surface and, to a lesser extent, the growth temperature. For example, Figs. 2(d)–2(l) indicate that a reasonably flat Ge/GaAs epilayer (even if some roughness on the atomic level is
present) can be grown at 580 °C on a moderately 2D GaAs(001)-(1×1) surface [as characterized in Figs. 2(a)–2(c)]. On the other hand, on a poorly ordered GaAs(001)-(1×1) surface [as manifested through diffused intensity distribution and weekly expressed streaks in the RHEED patterns in Figs. 4(a)–4(c)], a clearly very rough 3D layer grows at the same temperature, as follows from the transmission RHEED patterns in Figs. 4(d)–4(f). There is usually a tendency to lower the growth temperature in order to reduce the thermal budget and interdiffusion and segregation phenomena. However, growth at a lower temperature makes things worse. The substrate quality according to RHEED in Figs. 5(a)–5(c) is comparable to that displayed in Figs. 4(a)–4(c). Yet, the Ge layer is not only 3D, but this time, also contains defects (most probably planar, such as twins and stacking faults), as can be inferred from the 1/4 and 3/4 spots observed in the patterns in Figs. 5(d)–5(f). Growth at an even lower temperature of 400 °C results in a completely polycrystalline layer, as evident not only from Debye rings in the diffraction pattern of Fig. 6(a), but explicitly shown in SEM and AFM micrographs in Figs. 6(b) and 6(c), respectively.

It should be pointed out that the quality of the Ge/GaAs epilayer improves with thickness. The improvement can be visualized as the reduction of intensity modulation along the diffracted streaks, e.g., when going from Figs. 2(d)–2(f) to Figs. 2(j)–2(l). When comparing [110]-RHEED patterns in Figs. 4(d), 4(g), and 4(j), one can even detect the appearance of half-order streaks indicating the formation of the expected (1×2) and (2×1) superstructure and better atomic ordering at the layer surface.
**B. Si capping of the Ge/GaAs(001)-(1×1) layer**

As in the aforementioned case of Ge growth on GaAs, capping the so-grown Ge/GaAs(001)-(1×1) layer with Si, is also strongly dependent on the epitaxial quality of that Ge layer, in addition to the complexity involved in the large lattice mismatch (about 4%) between Si and Ge. This mismatch is sufficient to drive the so-called (S–K) transition in the growing Ge heteroepilayer on Si, where the growth becomes 3D after an initially 2D wetting layer attains some critical thickness. The latter is usually explained either by the stabilization of the undulating wave due to the lowering of the elastic energy at the ripple peaks at the expense of the increased surface energy relative to the planar layer (provided the conditions for the minimum wavelength are met), or by some sort of cooperative nucleation mechanism, where the discretely nucleating 3D islands undergo coalescence.

It should be noted that the former mechanism only accounts for rippling of the compressively stressed layers, such as Ge/Si, rather than of the Si/Ge layers, which are in the state of tension. Whatever the undulation origins might be, both models predict symmetrical distributions of the undulations in two perpendicular (110) directions, unlike what is shown in Fig. 3. The exact reasons for such unidirectional rippling are certainly intriguing, and are yet to be accounted for.

Layer roughening due to S–K or Volmer–Weber 2D-to-3D transition is expected with the increasing strained-layer thickness, and unavoidable (unless surfactants are used). However, roughness on a significantly larger scale results when Si is grown on the already rough, 3D Ge/GaAs layer, as shown in Figs. 4 and 5. RHEED patterns in Figs. 5(g)–5(i) exemplify the exact Si replication of the underlying Ge/GaAs layer [Figs. 5(d)–5(f)], and a similar rough Si layer [Figs. 4(k) and 4(l)] results even when growing on a slightly less rough Ge/GaAs [e.g., in Fig. 4(j), where a certain degree of streaking, including half-order streaks, are present in RHEED in spite of the 3D-like spots]. Similar results were obtained during growth at 600 °C.

**IV. DISCUSSION**

Due to excellent lattice match, the morphology, and epitaxial quality of the Ge layer on GaAs(001) depend only on the crystalline perfection of the GaAs substrate surface, provided the growth temperature is high enough to allow for sufficient adatom mobility on the surface (our findings that the growth temperature should be higher than 400 °C are in excellent agreement with those of Salazar-Hernández). Hence, the type of GaAs surface reconstruction is important in determining the type of bonding formed between the Ge and GaAs atoms. For example, as was already mentioned, the excess As on the c(4×4) surface makes it inferior for Ge growth when compared with the intrinsic (2×4)-reconstructed GaAs surface, where Ge can bond directly to the GaAs lattice. Unreconstructed, or bulk-truncated GaAs is expected to provide an excellent substrate for heteroepitaxy since the bonding is between the adatom and one element (As or Ga) only. Unfortunately, there is no experimental data available in literature to compare with the results obtained in this study. Generally speaking, bulk-truncated semiconductor surfaces are not energetically stable due to the high density of dangling bonds, and hence they reconstruct. However As-rich GaAs(001)-(1×1) surfaces have been experimentally synthesized and observed under UHV conditions. Therefore, although our experimental As-free preparation procedure would favor Ga, rather than As, termination, it does not seem likely (there is also evidence that Ga termination leads to a c(8×2) superstructure). Single-element (1×1) termination would also create homogeneity similar to the lattices of elemental semiconductors and, therefore, favorable conditions for the development of a (1×2) and (2×1) mixture, inherent to UHV-prepared bulk or epitaxial Ge and Si surfaces.

It would therefore be reasonable to expect our Ge/GaAs(001)-(1×1) layers to be of excellent quality, and the reason they are not is most probably related to the limitations of our preparation procedure. Upon heating GaAs to 580 °C, not only native oxide evaporates, but, if left for too long, it causes As desorption from the lattice, as well. Ultimately, excess Ga leads, in turn, to a massive formation of Ga droplets and a very rough 3D surface. In this work, an attempt was made to start Ge deposition immediately upon transition from a halo RHEED pattern into a streaked one, as demonstrated in Figs. 1 and 2. Apparently, the better surfaces, such as the ones in Figs. 2(a)–2(c), resulted in better Ge epilayers [see RHEED in Figs. 2(j)–2(l)]. On the other hand, when the beginning of growth was delayed and some Ga droplets formed, the surface of the substrate was rougher and so was the resultant epilayer, e.g., as can be judged from Figs. 4 and 5.

Capping the so-grown Ge/GaAs(001) layers with Si is, on the one hand, simpler because both Si and Ge are elemental and in many ways similar semiconductors and, on the other hand, more complicated by far due to the large mismatch between the two. In spite of such a mismatch, some models predict smoother epitaxial growth of Si on Ge, than vice versa. Classical mechanics of solids, which explains the roughening transition of the Ge epilayers on Si in terms of the buckling of a compressively stressed solid (see Sec. III B), cannot account for a similar type of roughening in a layer under tension. Another model attempts to describe the roughening by the reduction of step energies and the resultant proliferation of steps and step bunching. Due to the details of step structure in group-IV semiconductors, compression reduces the step energies, whereas tension increases them. However, the application of these and other models that account, for example, for roughening even in homoepitaxy to discretely nucleated nanoislands or ripples, seems doubtful.

Another problem in capping the Ge layers with Si is related to the surface energy considerations: The Ge surface energy for a (001)-(2×1) reconstruction is 0.07 eV/atom lower than for Si, the difference between Si and Ge dimer bonds is about 0.5 eV/atom, and the difference between unsaturated Si and Ge bonds is therefore (2×0.07+0.5)/2 =0.32 eV/atom. This explains the Ge segregation to Si cap surfaces, as well as the nucleation of 3D Si islands on Ge in accord with the Golden Rule of Epitaxy “If material B
wets material A, the latter would not wet the former”, because that would imply coagulation of material A into islands not to cover the lower-energy-material B. However, after the entire Ge surface is eventually covered with Si nanocrystals, the driving force for 3D growth (to maximize the area of a bare Ge surface) vanishes, and the morphology begins to flatten.

V. CONCLUSIONS

In this work, Ge and Si layers were epitaxially and consecutively grown on GaAs(001) substrates by electron-beam evaporation under UHV conditions. The central variable parameters were growth temperatures and layer thicknesses. One should note the simple way in which GaAs substrates were prepared, namely desorption of the native oxide at 580 °C in an As-free atmosphere, which significantly simplified the process in this study. These substrates exhibited a bulklike (1×1) termination.

Three major factors were found to have an impact on the Ge/GaAs(001) growth: (i) morphology and crystalline perfection of the GaAs substrate, (ii) GaAs surface reconstruction, and (iii) Ge growth temperature. In the 500 °C–600 °C temperature range, reasonable quality Ge epilayers can be grown, provided the surface of the substrate is not too rough. In this range, a certain amount of interdiffusion and segregation may take place, as was found by an x-ray photoelectron spectroscopy (XPS) depth profiling (not shown here). However, epitaxial growth at 400 °C is impeded by the insufficient surface mobility and the formation of polycrystalline film. The (1×1) bulk truncation of the GaAs substrates prepared by thermal cleaning in the As-free vacuum is predicted to create a good-quality epilayer, provided the deposition precedes the formation of Ga droplets on the surface. Otherwise, high substrate roughness is replicated by the epilayer. The reconstruction of flat Ge/GaAs(001)- (1×1) is the familiar (1×2) and (2×1) mixture, typical of group-IV semiconductor surfaces, and it persists in layers as thick as 100 nm.

Initially Si (or low-x Si<sub>1-x</sub>Ge<sub>x</sub>) capping layers replicate the morphology of the Ge layers in the same way as the Ge layers replicate the morphology of the underlying GaAs surface. In addition, due to the large lattice mismatch between Si and Ge, Si tends to form discrete 3D nanoislands or continuous ripples on Ge, which is why gradual strain relaxation by means of graded Ge<sub>1-x</sub>Si<sub>x</sub> buffers is required. Our experiments prove the viability of this method. For example, we have managed to grow Si<sub>0.8</sub>Ge<sub>0.2</sub> layer, which was strained almost to the same extent (3.2%) as pure Si layer (4%), up to a thickness of 100 nm, and capped it with a 50 nm thick pure Si layer at 480 °C, which greatly reduced Ge segregation and Si–Ge intermixing (according to XPS depth profiles). The flat portions of these two layers exhibited the same (1×2) and (2×1) reconstruction as the underlying Ge, even though half-order RHEED streaks could no longer be observed when the electron beam was incident normally to preferentially aligned surface ripples, which were formed by then. These ripples resembled strain-induced undulations in Ge/Si(001) layers. However, unlike those undulations, the ripples here were oriented preferentially along one of the (110) directions only. Such an anisotropy may originate at the crystallography of the GaAs(001) surface, namely the difference in bonding geometry between two unequivalent (110) directions. However, without detailed atomic-resolution studies of the initial stages of epitaxy, for example, with an STM, this would remain a mere speculation. It seems likely that, with the aid of graded buffers, starting from pure Ge (x = 0) and ending with pure Si (x = 1), high-quality Si epilayers can be grown on GaAs(001).

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