Strained-Layer Superlattices: Materials Science and Technology

Volume Editor Thomas P. Pearsall

SEMICONDUCTORS AND SEMIMETALS VOLUME 33 Treatise Editors: R.K. Willardson and Albert C. Beer

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SEMICONDUCTORS AND SEMIMETALS Volume 33

Semiconductors and Semimetals

A Treatise

Edited by R. K. Willardson

ENIMONT AMERICA, INC. PHOENIX, ARIZONA Albert C. Beer

BATTELLE COLUMBUS LABORATORIES COLUMBUS, OHIO

Strained-Layer Superlattices: Materials Science and Technology

SEMICONDUCTORS AND SEMIMETALS

Volume 33

Volume Editor

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Preface

During the last decade, it has been acknowledged that the technology of silicon integrated circuits is approaching fundamental limits set by the atomic nature of matter. It is no longer possible to count on a doubling of chip capacity every few years. At the same time, the telecommunications and recording industries have driven the development of an economical and reliable optoelectronics technology. Optoelectronics offers *new functionality* to conventional silicon-based circuits. Development and integration of this new functionality is essential to the continued expansion of the information processing capacity of integrated circuits. Yet a vast gulf continues to separate the technologies for optoelectronics and silicon-based devices because they are based on dissimilar materials. These two volumes (Volumes 32 and 33) on strained-layer superlattices are dedicated to the idea that this gulf will be short-lived.

In 1982 Gordon Osbourn of Sandia Laboratories made the link between strained-layer structures and the need for new functionality in integrated circuit design.¹ Osbourn considered the conventional wisdom that all strain in semiconducting devices was bad and stood it on its head by proposing that the strain associated with the heteroepitaxy of dissimilar materials may itself offer *new functionality*, whose advantages may far outweigh the disadvantages of the presence of strain. In 1986, Temkin *et al.*² tested a device that illustrates the possibilities opened up by this breakthrough in thinking: a silicon-based photodiode with an absorption edge, strain-shifted to the 1.3–1.5 μ m window for optical fiber communications.

The physics and technology of semiconductor strained-layer superlattices are surveyed in this two-volume set. Of course, the field of activity is wide and growing. The contents of this set should not be viewed as a review, but rather as a milestone in research and development that will play an important part in the evolution of semiconductor device technology.

> Thomas P. Pearsall March 28, 1990

^[1] Osbourn, G. C. (1982), J. Appl. Phys. 53, 1586.

^[2] Temkin, H., Pearsall, T. P., Bean, J. C., Logan, R. A., and Luryi, S. (1986), Appl. Phys. Lett. 48, 330.

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CHAPTER 1

Principles and Concepts of Strained-Layer Epitaxy

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I. Introduction

Atomic-scale growth control of artificially modulated structures by advanced crystal-growth techniques such as molecular-beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) has in the last decade

1

extended the frontiers of materials science, physics, and semiconductor device performance. Historically, the initial focus has been on the growth of material combinations with essentially the same crystal lattice parameter and structure, e.g., $Al_xGa_{1-x}/GaAs$. Although the growth of ultrahigh electrical and structural quality material in these and similar systems has required both perseverance and inspiration, the fundamental physical constraints on successfully defining the epitaxial structure (i.e., point and line defect free, with planar surface morphology) are greatly eased when the equilibrium structure of the grown layers corresponds closely to that of the substrate.

Interest in extending the range of possible material combinations has, however, encouraged experimentation in lattice-mismatched epitaxial structures. In addition to the problems encountered (and to a large extent, solved) in lattice-matched epitaxy, the primary extra complication introduced by this extra degree of freedom is the introduction of extended defects that attempt to relieve elastic strain in the structure. Understanding and control of these defects appears to be the principal challenge faced in strained-layer epitaxy, and progress to date will be discussed in detail later in this chapter. Other phenomena present in lattice-matched epitaxy, e.g., surface diffusion and clustering phenomena, may be more significant in mismatched-epitaxy, due to the likelihood of a greater chemical dissimilarity between materials in the structure. Indeed, we shall aim to show in this chapter that each and every stage in the heteroepitaxial growth process, from substrate preparation to post-growth processing, is of critical importance in determining the final structure.

The field of strained-layer epitaxial growth is very much in its formative stages and is continually evolving. Care will be taken in this chapter to attemt to differentiate among those problems that appear presently to be understood, those in which an understanding is being developed, and those that to date remain intractable. The following fundamental stages of the heteroepitaxial growth process should be considered:

(i) Construction of a suitable growth chamber;

(ii) Preparation of the substrate surface;

(iii) Possible growth of a homoepitaxial buffer layer onto the as-cleaned substrate surface;

(iv) Nucleation of the heteroepitaxial layer: clustering or layer-by-layer growth;

(v) Introduction of extended defects (if critical-layer dimensions are exceeded) to relax the elastic strain introduced by lattice mismatch;

(vi) Evolution of the growth surface, i.e., coalescence of individual nuclei, or possibly roughening of a planar surface. Note that this stage could occur before or after step (v); and

(vii) Redistribution of defect populations within the epitaxial layer, such as by defect "filtering" via incorporation of strained-layer superlattices or termination of a dislocation at the edge of a structure.

Each of these processes will be discussed in succeeding sections of this chapter. Our aim will not be to review exhaustively all work done in the field (specific materials systems are reviewed in other chapters of this volume), but rather to outline the fundamental physical processes involved in strainedlayer epitaxy and to illustrate them with specific examples.

II. Growth Techniques

A. INTRODUCTION

The fundamental tool of lattice-mismatched epitaxy is the crystal-growth chamber. The major requirements of a growth chamber for high-quality epitaxial growth include: a noncontaminating (ultrahigh vacuum or inert) environment; source purity; a source-substrate geometry that allows deposition uniformity; uniform substrate heating/cooling; absence of particulates and undesired impurity atoms; sufficient analytical techniques to allow in situ monitoring of growth quality and control of layer composition and thickness. In a research environment, throughput of wafers is less critical, vacuum (UHV) techniques, particularly solidtherefore ultrahigh evaporation-source MBE, are acceptable. MBE has two relevant advantages: (1) exceedingly good control of layer dimensions and composition; (2) growth at minimal temperatures (generally well below those required for significant bulk diffusion but not necessarily surface diffusion). Low-temperature growth is an absolute requirement if one is to attempt metastable strained-layer epitaxy (as in the germanium silicide system).

The following sections give a brief overview of the crystal growth techniques being used for strained-layer growth including molecular-beam epitaxy, atomic-layer epitaxy, gas-source molecular beam epitaxy and chemical vapor deposition (CVD). However, in subsequent sections, discussion will tend to focus on MBE. This is justified by the current dominance of MBE in strained-layer epitaxy and by the fact that, with MBE, it is particularly straightforward to define the role of substrate preparation, impurity effects, and nucleation. Nevertheless, the reader should bear in mind that these issues and discussions are generic to all crystal growth techniques.

B. MOLECULAR-BEAM EPITAXY AND ATOMIC-LAYER EPITAXY

Some important principles of the MBE growth technique are illustrated in Figs. 1a and 1b. The essential requirement for a MBE growth chamber is that







FIG. 1. Schematic diagram of a molecular-beam epitaxy growth chamber (a) for column-IV deposition, (b) for III-V deposition.

growth take place at a sufficiently high vacuum so that arrival and sticking of impurity atoms from the ambient occur at a negligible rate. This is particularly important in the growth of strained-layer heteroepitaxy. On growing surfaces, impurities can massively perturb growth by providing heterogeneous cluster or defect nucleation sites. Within the crystal, impurities may precipitate to form nucleation sites for strain-relieving dislocations.

To first order, impurity gas impingement varies inversely with partial pressure with a pressure of 10^{-6} torr producing a flux of 1 atomic monolayer per second. Thus, a total chamber pressure of 10^{-10} torr corresponds to an arrival rate of $\sim 10^{-4}$ atoms or molecules sec⁻¹ cm⁻² on the growth surface. For typical MBE growth rates of ~ 1 monolayer sec⁻¹, this relatively low arrival rate would still produce an unacceptably high impurity concentration in the growing epilayer, were the sticking coefficient for the impurities unity.

Fortunately, at the elevated temperatures (of the order of 700–1200 K) generally employed during substrate cleaning and epilayer growth, sticking coefficients for most UHV constituents are many orders of magnitude less than one, permitting high purity growth. However, there are exceptions, and these exceptions strongly affect the design of the MBE growth chamber. In particular, growing AlAs and AlGaAs alloys have an extremely strong affinity for oxygen derived from the strength of the oxygen–aluminium chemical bond. Oxygen can affect layer morphology and electronic carrier transport. In a leak-free MBE system, this oxygen comes from decomposition of ambient water vapor held over from earlier venting of the vacuum chamber. This can be largely eliminated by the addition of extensive internal shrouds filled with liquid nitrogen on which the water is trapped. With the advent of plumbed-in liquid-nitrogen supply systems, these shrouds are frequently cooled not only during growth but continuously, over months of operation.

The strength of the carbon-silicon bond poses a similar problem in MBE of silicon and silicon alloys. Although carbon is relatively soluble in silicon, its presence at a growing crystal surface can lead to the formation of silicon carbide nuclei. These nuclei are extremely stable and, given their hexagonal crystal structure, they provide ready sites for defect nucleation in the cubic silicon lattice. Carbon can come from several sources. It is present in all but the most carefully controlled chemical cleaning solutions. Even if such control is maintained, an atomically clean surface will immediately react with carbon in ambient air. Ex situ cleaning is therefore generally terminated with the formation of a comparably inert chemical oxide that can be readily reduced and desorbed by heating in vacuum. While such surfaces are adequate for basic studies of silicon homoepitaxy, residual carbon can still adversely affect heteroepitaxial nucleation and strained-layer relief, as detailed later.

Carbon may also come from the decomposition of oils used in certain vacuum pumps. In the last decade or so, such pumps had been largely eliminated in favor of oil-free ion pumps and closed-cycle He cryogenic condensation pumps. Recently, however, manufacturability issues have stimulated renewed interest in gas-source MBE or MBE/CVD hybrid vacuum technologies. Ion pumps cannot handle significant gas loads, and the accumulation of typical gas-source chemicals within cryogenic pumps poses both toxic hazards and the possibility of ignition and/or explosion. Gassource systems must therefore use nonaccumulating pumps such as diffusion pumps or turbo-molecular pumps. Carbon contamination from such pumps proved to be the bane of early attempts at silicon MBE (Joyce, 1974). The challenge is thus to develop hydrocarbon trapping techniques and chemically resistant oil-free fore-pumps. Whereas this might appear to be a problem unique to silicon MBE, the handling of fore-pump oils contaminated with HI-V toxic materials is already a significant safety concern. At least one organization is already recommending the elimination of conventional oil fore-pumps on all gas-source systems.

Ironically, the reduction of oxygen and carbon contamination in solidsource MBE systems has introduced another defect-producing mechanism: particulates. In a solid-source MBE system (or a hot-wall CVD-like system), material will deposit in areas other than the targeted substrate. If vacuum is maintained for long periods, the buildup of material will produce strains leading to fracture and the release of very fine particulates. (Gross flaking may also occur, but it poses less of a problem.) Under the influence of applied electric fields or even typical MBE vapor fluxes, these particulates can actually be propelled upward onto a growing epitaxial surface (Matteson and Bowling, 1988).

Uncontrolled, these particulates can produce defect densities of 100–1000 per square centimeter (Bellevance, 1988). There are two emerging strategies to control this problem. This first is to tightly columnate the deposition fluxes to the substrate surface alone. The columnators are then replaced or cleaned of accumulated deposits at each vacuum break. The second approach is to grossly reduce thermal cycling within the MBE chamber, thereby maximizing deposit adhesion. In AlGaAs systems, this is accomplished by continuous cooling of liquid-nitrogen shrouds. In silicon-based MBE systems, the newest generation of equipment goes one step further. Because oxygen does not bond strongly to heated silicon, water vapor is not as critical a concern. Liquid-nitrogen shrouding is thus being removed from the growth area in favor of water cooling of either shrouds or chamber walls (e.g., Parker and Whall, 1988).

Assuming one can provide a suitably clean environment for molecularbeam epitaxy, the next problem is that of controlling layer composition. In an alloy system, such as Ge_xSi_{1-x} , significant errors may be tolerable. Growth of compounds, e.g. GaAs, however, requires control of stoichiometry to levels better than one part per million. If such control is not maintained, secondphase inclusions will form and crystal growth will be massively disrupted. Figures 1a and 1b illustrate typical schemes for the growth of III-V and column-IV materials, respectively. Neither temperature-controlled Knudsen cells, mass-flows-controlled gas sources, nor sensor-controlled electron guns offer the requisite part-per-million regulation.

MBE thus depends on one of two mechanisms to maintain stoichiometry. For common III-V semiconductors, it was found that although the column-V species will bind tightly to a freshly deposited column-III layer, it will not bond well to another column-V layer. In terms of GaAs, this is to say that As will bind to Ga but tends to re-evaporate from another layer of As. Stoichiometry is thus maintained if one provides an excess flux of the column-V species. The crystal then adsorbs only the species it requires.

Atomic-layer epitaxy (ALE) simply takes this process one step further: For example, in growth of certain II-VI semiconductors, the complementary process is also active, and whereas column-II materials will bind to column VI, neither will bind to itself (at appropriate growth temperatures). Growth rate is then independent of the incoming flux and depends only on the number of times the substrate is exposed to alternate pulses of column-II and VI atoms (as each pulse produces a single, self-limiting atomic layer of deposition). This self-balancing process is essentially the same as that active in liquid-phase epitaxy or chemical vapor deposition.

The second self-balancing mechanism is operative in MBE growth of compounds such as $CoSi_2$ on Si. Neither Co nor Si will re-evaporate, but excess Co will readily diffuse through a thin $CoSi_2$ layer to react at the silicon substrate. In essence, stoichiometry is achieved by simultaneous vapor-phase crystal growth at the surface and solid-phase growth at the substrate. Excess metal fluxes may thus be used in thin layers, but as the epilayer thickness increases, diffusive transport of Co through the epilayer becomes increasingly difficult, and growth will ultimately break down.

C. GAS-SOURCE MOLECULAR-BEAM EPITAXY

For the purposes of this chapter, gas-source MBE (GSMBE) can be considered a simple derivative of the solid-source process. Gas sources address three weaknesses of conventional MBE. First, Knudsen evaporation sources have a finite capacity (of the order of 50–100 cc) and may be depleted within as little as a month. This is particularly true for the column-V species, where excess fluxes must be maintained in order to assure stoichiometric growth of a III–V compound. Further, before a cell is fully depleted, there will be serious shifts in evaporation rates due to the reduction of charge size. To compensate for this, frequent, sacrificial calibration runs must be made, and for very critical structures, the shift of calibration within a single run may become unacceptable. The use of external, easily replaceable, gas cylinders eliminates this problem. Fluxes are continuously calibrated and regulated by mass-flow controllers or temperature baths. Moreover, the elimination of vacuum breaks not only increases chamber up-time but can result in a significant overall reduction of vacuum impurity levels.

Gas sources have a second advantage in that they overcome difficulties in handling pyrophoric species such as white phosphorus. Phosphine, although highly toxic, is not spontaneously flammable and with proper handling will not accumulate within the MBE system. This has opened the door to the highly successful growth of GaInAsP species by MBE.

Finally, with certain chemistries and growth temperatures, the species from gas sources may decompose at the heated substrate surface alone. There will be little or no wall deposition, and the elimination of such accumulations will largely eliminate particulate contamination due to flaking. Although not currently recognized as an issue in III-V MBE, it has been shown that solid-source wall deposits can limit silicon MBE materials to defect densities of above 100–1000/cm², as discussed earlier.

D. CHEMICAL VAPOR DEPOSITION

Turning history around a bit, CVD can be viewed as a high-pressure variant of gas-source MBE (GSMBE). The chemistries are fundamentally similar; the differences depend primarily on what is done with the gaseous species. In CVD, gaseous species are delivered to the substrate wafer in their original form, that is, as column-V hydrides or column-III organics. In GSMBE, the hydride is often thermally "cracked" into a subhydride or pure column-V species by passing through a heated nozzle (often including a catalyzing metal). For the purposes of this chapter, the major possible advantage of this cracking process is that it can permit growth of epitaxy at lower substrate temperatures. This could be important if one is attempting to maintain strained-layer epitaxy to thicknesses above equilibrium limits. The reduction of temperature would then inhibit nucleation and growth of defects and thus reduce the relaxation of strain. However, to date, such metastable growth has only been well documented in the GeSi system. Thus, for the bulk of III-V growth, the absence of precracking places CVD at no significant disadvantage, and enhancements in wafer size and sample preparation may actually make it more desirable than MBE for the bulk of III-V growth systems.

III. Importance of the Substrate Surface in Heteroepitaxial Growth

The initial stage of the deposition process is to obtain a suitable surface on which to initiate growth. The primary concern is to obtain a surface that is atomically clean, i.e., stripped of its native oxide and free of any other surface or near-surface contaminants. To prevent reoxidation or contamination of the cleaned surface, at least the final stages of the cleaning process are usually done in situ under UHV conditions.

In general, the requirements for cleaning elemental column-IV substrates are more stringent than those for cleaning of III-V-compound semiconductor substrates. This is driven both by technological requirements and by the fact that native oxides desorb at significantly lower temperatures for the latter class of materials. By current standards, an adequate GaAs substrate can be prepared by ex situ wafer degreasing, followed by in situ oxide desorption at $\sim 600^{\circ}$ C and growth of a homoepitaxial buffer layer. To produce state-ofthe-art Si epitaxy, much more ingenuity and care are required. Tendencies toward islanded growth also make silicon substrate preparation a major issue in strained-layer growth of disparate materials such as GaAs on Si.

Conventional silicon substrate cleaning techniques fall into three general classes: (i) ex situ chemical cleaning followed by growth of a relatively volatile surface $SiO_x(x \sim 1)$ layer, followed by in situ desorption of the volatile oxide, this occuring at much lower temperatures than for the native SiO_2 oxide; (ii) in situ removal of the surface and near-surface region by sputtering with inert (generally argon) ions, followed by a thermal anneal to remove sputtering damage; (iii) in situ back-etching of the substrate under chlorine gas to remove several hundred angstroms of material. Only the later back-etching technique has demonstrated quality adequate for commercial production of complex integrated circuits. Unfortunately, its use is restricted to halogen CVD growth, and virtually all the work in this book is based on the first two approaches.

In the first class of cleaning techniques, the major requirements are first to chemically strip the Si-substrate surface in a manner that does not leave any detectable contaminants, especially carbon or metallic species, second, to produce a volatile oxide layer of uniform stoichiometry and thickness, and third, to successfully desorb the volatile oxide in situ in the growth chamber. None of these requirements are easy to satisfy. A variety of chemical cleaning techniques have been developed to satisfy the first two requirements above, e.g., the Henderson (1972) and Shiraki-Ishizaka (Ishizaka et al., 1983) cleans. The latter treatment is most widely used and consists of repeated oxidation and stripping of the surface in nitric and hydrofluoric acids, respectively, followed by growth of an approximately 10-Å-thick SiO layer in a hydrogen peroxide-hydrochloric acid mixture. In the original reference, it was suggested that desorption temperatures as low as 750°C would be sufficient to produce an oxygen-free surface; it has been our experience and that of others (e.g., Xie *et al.*, 1986) that somewhat higher temperatures (> $\sim 900^{\circ}$ C) are required to produce truly clean surfaces using this technique. This is illustrated by secondary ion mass spectroscopy (SIMS) data showing the residual surface contamination following Shiraki oxide desorption at various temperatures in Fig. 2.



FIG. 2. Secondary ion mass spectroscopy of residual O and C surface contamination following Shiraki cleaning of Si(100) wafers at various SiO desorption temperatures (from Xie *et al.*, 1986).

A number of variants of the basic Henderson and Shiraki methods have been developed. Oxide desorption has been shown to be more effective when a Si flux impinges upon the surface (Tabe *et al.*, 1981; Hardeman *et al.*, 1985), presumably because pockets of O-rich SiO_x can be converted to the correct monoxide stoichiometry. Another variant involves ozone cleaning under ultraviolet irradiation between the volatile oxide growth and desorption stages (Tabe, 1984); this technique has been shown to be extremely effective at reducing surface organic contaminants, reducing homoepitaxial defect densities by ~ 2 orders of magnitude on Si(100) and (111) surfaces for desorption temperatures of 800–900°C.

The second major class of cleaning techniques consists of in situ sputtering with inert gas ions to remove the near-surface region. In our laboratory, Si surfaces are cleaned using $\sim Ar^+$ ions accelerated to 0.2 keV, with the substrate held at room temperature. Approximately 100 Å of material is removed, leaving a clean but disordered surface. The substrate is then annealed at 750°C for five to fifteen minutes. The amorphous surface layer reorders by solid-phase epitaxy as the sample passes through 500-600°C, and residual point defects are annealed out at 750°C. Defect densities in homoepitaxial layers grown upon these cleaned surfaces are of the order of 10^2-10^3 cm⁻², comparable to or better than Shiraki-type cleaning techniques at 800°C.

A recently developed cleaning technique (Grunthaner *et al.*, 1988) offers promise of clean Si surfaces at far lower temperatures. This process involves ex situ removal of a thin 10 Å chemical oxide by spinning in a N₂ dry box loadlocked to the MBE chamber, while rinsing/etching first in pure ethanol (added dropwise), then in 1:10 HF:ethanol, and finally in pure ethanol. This technique produces an atomically clean (to a level at least comparable to standard in situ volatile oxide desorption at temperatures of ~ 800°C) hydrogen-passivated 1 × 1 surface after heating to 150°C. Conversion to a 7 × 7 reconstruction on a (111) surface occurs at temperatures of ~ 500°C.

Although further improvements in Si cleaning techniques are both preferable and possible, it appears that careful control of these processes can produce Si surfaces that are sufficiently clean to allow high-quality heteroepitaxial growth upon them. An area that has hitherto received little attention, however, is the effect of the substrate cleaning on surface morphology and the resultant heteronucleation stage. For growth on Si substrates, we have observed that both major classes of cleaning techniques can affect the surface morphology and influence the initial stages of heteroepitaxial growth.

In Fig. 3, we show high-resolution cross-sectional transmission electron microscope (TEM) images of the early nucleation stages of GaAs grown on a Si substrate cleaned by the Ishizaka process (for exact details, see Koch *et al.*, 1987). The substrate orientation is with the surface normal 4 degrees from



(b)

FIG. 3. (a) Cross-sectional TEM images of GaAs nucleation onto a vicinal (4 degrees toward $\langle 011 \rangle$)Si(100) wafer following SiO desorption at 880°C for 20 minutes. Note nucleation of GaAs on surface facets (arrowed) (from Hull *et al.*, 1987b); (b) lattice structure image of one facet (from Hull *et al.*, 1987a, b).

[100], the direction of the misorientation being towards an in-plane $\langle 011 \rangle$ azimuth. Growth of GaAs on such misoriented wafers historically believed to produce a uniform array of (200) steps on the Si surface, which prevents the formation of antiphase boundaries at the GaAs-Si interface (e.g., Kroemer, 1986).

From the images of Fig. 3, we note, however, that the Si substrate surface does not consist of a regular array of (200) steps and (100) terrace, but rather