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Managing Editor
Dr. Claus E. Ascheron
Springer-Verlag GmbH
Tiergartenstr. 17
69121 Heidelberg
Germany
Email: claus.ascheron@springer.com

Assistant Editor
Adelheid H. Duhm
Springer-Verlag GmbH
Tiergartenstr. 17
69121 Heidelberg
Germany
Email: adelheid.duhm@springer.com
Materials science is the prime example of an interdisciplinary science. It encompasses the fields of physics, chemistry, material science, electrical engineering, chemical engineering and other disciplines. Success has been outstanding. World-class accomplishments in materials have been recognized by Nobel prizes in Physics and Chemistry and given rise to entirely new technologies. Materials science advances have underpinned the technology revolution that has driven societal changes for the last fifty years.

Obviously the end is not in sight! Future technology-based problems dominate the current scene. High on the list are control and conservation of energy and environment, water purity and availability, and propagating the information revolution. All fall in the technology domain. In every case proposed solutions begin with new forms of materials, materials processing or new artificial material structures. Scientists seek new forms of photovoltaics with greater efficiency and lower cost. Water purity may be solved through surface control, which promises new desalination processes at lower energy and lower cost. Revolutionary concepts to extend the information revolution reside in controlling the “spin” of electrons or enabling quantum states as in quantum computing. Ion-beam experts make substantial contributions to all of these burgeoning sciences.

A striking feature of modern technology is the important role of the surface and near-surface regions of materials. Modern communications, complex data storage, electronic thin-film displays, biochips, digital cameras are products of innovative research employing surfaces and thin films in new and creative ways. Ion-beam technology provides a unique and exciting way of modifying the near-surface region of a solid; controlling its surface properties, adding beneficial impurities in the near-surface region, modifying the crystallinity, and providing a control and specificity that exceeds almost all other methods of surface modification. Ion-beam science and engineering have already made extraordinary impacts in current silicon technology for communications, surface hardening for structural improvements and materials modification to create solids with new properties. In addition, ion-beam science has emerged as one of the principal ways of quantifying surfaces, through a subfield known as ion-beam analysis. This background and accomplishment, and the use of these analytical tools, now comprise the underpinning for
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Ion-Beam-Induced Amorphization and Epitaxial Crystallization of Silicon

J.S. Williams\textsuperscript{1}, G. de M. Ázevedo\textsuperscript{1,2}, H. Bernas\textsuperscript{3} and F. Fortuna\textsuperscript{3}

\textsuperscript{1} Research School of Physical Sciences and Engineering, Australian National University, Canberra, 0200, Australia, e-mail: jsw109@rsphys1.anu.edu.au
\textsuperscript{2} Present address: Brazilian Synchrotron Light Laboratory (LNLS), 6192 CEP, 13084-971, Campinas, SP, Brazil
\textsuperscript{3} CSNSM-CNRS, University Paris-Sud 11, 91405 Orsay, France

\textbf{Abstract.} Ion-induced collisions produce athermal atomic movements at and around the surface or interface, inducing step formation and modifying growth conditions. The latter may be controlled by varying the temperature and ion-beam characteristics, guiding the system between nonequilibrium and quasiequilibrium states. Silicon is an ideal material to observe and understand such processes. For ion irradiation at or below room temperature, damage due to collision cascades leads to Si amorphization. At temperatures where defects are mobile and interact, irradiation can lead to layer-by-layer amorphization, whereas at higher temperatures irradiation can lead to the recrystallization of previously amorphized layers. This chapter focuses on the role of ion beams in the interface evolution. We first give an overview of ion beam-induced epitaxial crystallization (IBIEC) and ion-beam-induced amorphization as observed in silicon and identify unresolved issues. Similarities and differences with more familiar surface thermal growth processes are emphasized. Theories and computer simulations developed for surface relaxation help us to quantify several important aspects of IBIEC. Recent experiments provide insight into the influence of ion-induced defect interactions on IBIEC, and are also partly interpreted via computer simulations. The case of phase transformations and precipitation at interfaces is also considered.

\textbf{1 Introduction}

Possibly the most important feature of surfaces is their irregularity: crystals only grow, when matter is added, because steps form on the surface. These may be due to the deposited adatoms, or/and to sample heating – the step free energy is reduced as the configurational entropy term increases \cite{1}. Another way to induce step formation and modify growth conditions involves charged-particle irradiation: ion-induced collisions produce athermal atomic movements at and around the surface or interface, and these (and hence the configurational entropy) may be controlled to some extent by varying the irradiation conditions. Performing the irradiation at different temperatures provides a potentially powerful means of guiding the system between nonequilibrium and quasiequilibrium states. Several such effects at surfaces are discussed in the chapter “Spontaneous Patterning of Surfaces by Low-Energy

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Ion Beams” by Chason and Chan. In this chapter, we examine a situation in which, because they penetrate inside matter, ion beams play an even more specific role: that of growing interfaces. The latter display both similarities to and differences from surface evolution, notably as concerns phase transformations and precipitation at interfaces. We shall emphasize the cases of ion-beam-induced epitaxial crystallization (IBIEC) and ion-beam-induced amorphization. The topic emerged as a typical materials-science problem, in which basic and applied physics are totally intertwined. A near-surface amorphous layer and hence a buried crystal/amorphous interface can be produced in a silicon matrix by ion implantation (say, of a dopant). Recrystallization of this amorphous layer may be induced by high-temperature annealing (solid-phase epitaxial growth, SPEG), a quasiequilibrium technique, or by IBIEC. In the latter, the ion beam provides the atomic displacement energy, so that IBIEC occurs in a temperature range (typically around 200–400°C) some 200–400 degrees below SPEG. This can be advantageous for applications, since it is far more compatible with the preservation of prior microelectronics fabrication steps in an industrial environment.

Experimental studies show that under both SPEG and IBIEC the initially blurred, defected interface is first smoothened, then progressively moves towards the surface. The SPEG mechanism has been modeled [2] in thermodynamical terms as a sequence of bond rearrangements at the interface. This will be summarized later in order to provide a reference for specific ion-beam effects, but first we very briefly indicate some of the main ideas to which our discussion relates. When adatoms are deposited on surfaces at high temperatures, steps form and flow; in the intermediate temperature range where limited atomic motion occurs on the surface after deposition, nucleation, growth and island coalescence occur. Growth is the result of adatoms reaching step edges from above or below, with correspondingly different energy barriers (and activation energies). At temperatures sufficiently low to hinder any long-range atomic motion, deposition may lead either to formation of an amorphous deposit or to local epitaxy, depending on the latent heat and kinetic energy released by the arriving atom. It is known [3, 4] that atom deposition or ion bombardment at hyperthermal energies enhances the kinetic energy component, leading to an effective “local annealing” that favors short-range epitaxial growth by a well-defined bond rearrangement. On the other hand, the overall surface roughness increases progressively as inhomogeneities produced by random deposition of atoms or islanding interfere with each other’s lateral expansion. Since this process multiplies the number of steps, it enhances the growth speed for a given deposition density. In the case of ion irradiation, how then do surface growth models relate to ion-irradiation-induced interfacial growth? The latter’s evolution does not involve any increase in the amount of matter (no adatoms). However, the interface moves and its roughness is modified, its overall shape becoming “more planar”. This signals the existence of interface relaxation, implying that matter
has effectively moved along the interface. Do atoms move (by random or non-
random diffusion) on the interface, or are the atomic movements limited to
local bond restructuring and subsequent relaxation? If the latter is correct,
can one specify the relaxation mode? This is where the theories developed
for surface relaxation may help us to quantify several important aspects of
SPEG and IBIEC, as we will see in Sect. 4.

Let us first consider some of the main experimental features. When mate-
rials are irradiated with energetic ions, the ion-induced disorder can lead to a
number of structural transformations, including amorphization and crystal-
ization. The behavior is particularly interesting when irradiation is carried
out at temperatures where the mobility of defects produced by the ion beam
is progressively increased. Silicon is an ideal material to observe and under-
stand such processes but, despite extensive studies over the past two decades,
there are still unanswered questions relating to ion-induced defects and their
influence on amorphization and crystallization.

For ion irradiation at or below room temperature in silicon, the disor-
der produced is essentially stable since point defects are readily immobi-
lized within disordered regions. Under such conditions, ion damage generated
within collision cascades builds up with ion dose, leading to amorphization of
the silicon. At higher implant temperatures, where defects begin to move and
interact during ion bombardment, significant defect annihilation can occur
and it can be difficult to induce amorphization. In this regime, preferential
amorphization can be observed at regions where extended defects first form,
for example, at nanocavities or at surfaces [5]. Continued irradiation can lead
to layer-by-layer amorphization, but at higher temperatures ion irradiation
may not cause amorphization. Incomplete defect annihilation during bombard-
ment can lead to the formation of defect clusters and even extended de-
fects in an otherwise crystalline matrix. In this elevated temperature regime,
where defects are mobile, the understanding of the observed defect-mediated
processes is far from complete. Irradiation at even higher temperatures can
even lead to the recrystallization of previously amorphized layers. The latter
IBIEC process occurs at temperatures well below those at which normal ther-
mal-induced crystallization of amorphous silicon occurs. IBIEC has been
shown to be an activated process, dependent on the generation of mobile
‘defects’ through atomic displacement during ion irradiation. There has been
considerable controversy as to the role of defects in IBIEC but recent exper-
iments have partly clarified this issue. Indeed, studies of ion-beam-induced
amorphization (IBIA) and IBIEC not only indicate much about the behavior
of defects and defect-induced phase changes in silicon but also provide
considerable insight into the fundamental physics of defect interactions and
epitaxial crystallization at the atomic level.

This review first gives an overview of ion-induced amorphization and crys-
tallization phenomena that have been observed in silicon and identifies some
unresolved issues. More recent experiments, that provide insight into both
ion-induced defect interactions and IBIEC, are then presented and partly interpreted with the aid of computer simulations. Finally, a summary of what is known and what is not known in these areas is presented.

2 Overview of Ion-Beam-Induced Amorphization

2.1 The Effect of Temperature on Defect Accumulation

At sufficiently low irradiation temperatures, residual lattice disorder in semiconductors is controlled by the energy deposited by swift ions in nuclear collisions with lattice atoms. Individual heavy ions can generate dense displacement cascades (Fig. 1a) that result directly in amorphous zones [6] and the overlap of such zones with increasing dose leads to a continuous amorphous layer [7, 8] as shown in the cross-sectional transmission electron micrograph (XTEM) in Fig. 1b. For light ions, cascades are less dense and the lattice can collapse to an amorphous phase when a sufficiently high defect density builds up and the local free energy of the defective lattice exceeds that of the amorphous phase [9-11]. These two extremes of damage build up at low temperatures can be successfully treated by heterogeneous (heavy ion) or homogeneous (light ion) models, such as those of Morehead and Crowder [7] and Vook and Stein [10], respectively.

![Fig. 1. (a) Schematic of displacements within a collision cascade. (b) A cross-sectional transmission electron microscope (XTEM) image of a continuous amorphous layer (a-Si) generated in silicon by 245-keV Si ion irradiation at room temperature to a dose of $3 \times 10^{15}$ cm$^{-2}$. The sample surface is indicated, as is the underlying crystalline silicon (c-Si).](image-url)
Fig. 2. XTEM images corresponding to 245-keV Si ion irradiation of silicon (100) to a dose of $4 \times 10^{15} \text{cm}^{-2}$ at (a) room temperature, and (b) $350^\circ \text{C}$. After [12]

The implantation temperature can determine whether the defects generated within collision cascades are stable or whether they can migrate and annihilate. An example of temperature-dependent effects is shown in Fig. 2 [12]. Figure 2a is a XTEM micrograph depicting a continuous amorphous layer in silicon, produced by 245-keV Si ions at room temperature to a dose of $4 \times 10^{15} \text{cm}^{-2}$. The ion range is around 3800 Å but, under these implant conditions, the amorphous layer is around 5000 Å thick.

Note that the boundary between the amorphous layer and the underlying silicon substrate is quite sharp. This may reflect the fact that defects produced in the tail of the Si implant distribution can annihilate quite effectively at this implant temperature and/or that there is an effective ordering correlation length or 'collective effect' operating on the crystalline side of the interface during irradiation. If the implant temperature is raised to $350^\circ \text{C}$, irradiation-produced defects are considerably more mobile and annihilate or cluster to effectively suppress amorphization [13], as shown in the XTEM micrograph in Fig. 2b. Here, there are clearly observed interstitial clusters that evolve into well-defined interstitial-based line defects such as $\{311\}$ defects and dislocation loops [14] on annealing. It will be shown later that, at
such implant temperatures where defects can annihilate, irradiation-induced displacements can induce crystallization of pre-existing amorphous layers.

Between the two extreme regimes illustrated in Fig. 2, the close balance between the rate of damage production within collision cascades and the rate of dynamic annealing (defect annihilation and clustering) can give rise to interesting defect-mediated phenomena, with strong dependencies on implantation temperature, dose and dose rate. Small changes in any of these parameters can result in dramatic differences in residual implantation damage from almost damage-free structures, as a result of efficient defect annihilation, to continuous amorphous layers. In this regime, amorphization can occur in an entirely different way, as a result of nucleation-limited or preferential amorphization processes [15]. For example, as the implantation dose increases and the density of defects increases, amorphous layers can spontaneously form at the depth of maximum disorder. Such layers can then grow to encompass the entire defective region [16]. Further examples of the critical balance between defect creation and defect annihilation, including preferential amorphization, are given below.

2.2 Preferential Amorphization at Surfaces and Defect Bands

Amorphous layers can be observed to nucleate preferentially at depths significantly away from the maximum in the ion's energy deposition distribution, at, for example, surfaces [17], interfaces and pre-existing defects [16, 18]. Figure 3 illustrates the case of preferential amorphization at a silicon surface or, more precisely, at a SiO$_2$–Si interface. Figure 3a [16] shows an RBS/channeling spectrum for an 80-keV Si implant into silicon at 160°C (dose $10^{16}$ cm$^{-2}$ at a beam flux of $2.7 \times 10^{13}$ ions cm$^{-2}$ s$^{-1}$).

The spectrum shows a strong disorder peak at the surface and a buried peak around the end-of-ion-range at about 1200 Å. (The end-of-ion-range refers to the region in the tail of the ion-range distribution, about two standard deviations deeper than the projected ion range.) The corresponding XTEM micrograph in Fig. 3b [16] indicates that there are two amorphous layers present, one extending 300 Å from the surface and a buried layer from 500 to 1500 Å. Between these layers is a region of crystalline silicon containing few defects, but below the buried layer there is a region of crystalline silicon that is rich in (interstitial-type) defect clusters. This result shows not only the nucleation of an amorphous region around the maximum in the nuclear energy distribution at about 800 Å but nucleation of an amorphous layer well away from the maximum disorder depth, at the surface. When the evolution of this defect structure was examined as a function of ion dose [16] it was found that the deep disorder first accumulated by forming defect clusters of interstitial character at lower doses. This defective region then appeared to collapse into an amorphous layer as the dose increased. In addition, the surface amorphous layer was found to thicken with increasing dose. This behavior suggests that, in a regime where substantial dynamic annealing occurs
during ion irradiation, mobile defects not only annihilate and locally form defect clusters, but can also migrate to and accumulate at SiO$_2$–Si interfaces. Collapse of such disorder to an amorphous phase can occur at a sufficiently high implantation dose. It has also been shown that a pre-existing dislocation band can act as a nucleation site for amorphyization, even when it is situated well away from the disorder peak [15]. Furthermore, such dislocation bands have also been found to ‘getter’ interstitial-based defects formed deeper in the material during irradiation [15]. Thus, it would appear that both dislocation bands, surfaces (actually SiO$_2$–Si interfaces) and amorphous layers themselves are good trapping sites or sinks for mobile defects that may otherwise form stable clusters close to where they come to rest, in the absence of such sinks. When defect accumulation occurs at such interfaces, amorphous layers can be observed to “grow”.

2.3 Mechanisms of Amorphization: The Role of Defects

The mechanism for the above defect trapping and preferential amorphization behavior deserves some comment. There has been considerable speculation
in the literature [13, 15, 19, 20] as to the specific defects that are trapped at pre-existing defects, surfaces and amorphous layers. Clearly, open-volume defects such as vacancies or divacancies, as well as interstitials or interstitial complexes, are candidates. As we discuss more fully below, some experiments on the kinetics of amorphous layer formation, in the regime where the irradiation-induced amorphous phase is nucleation limited, have suggested that divacancies [19] may be the main defects preferentially trapped at amorphous layers. However, other experiments, where amorphous layers are nucleated at pre-existing dislocation bands, suggest [15] that interstitial trapping also may have a major role to play. Regardless of the specific defects that accumulate prior to amorphization, it would appear that the local free energy plays a major role in determining the collapse of a defective crystalline lattice to the amorphous phase. This free-energy mechanism [21] is illustrated schematically in Fig. 4. In the case of silicon, the free energy of an amorphous phase exceeds that of a crystalline phase and there is a strong driving force for amorphous regions to crystallize. However, the amorphous phase is metastable since there is a kinetic barrier that must be overcome before crystallization can occur. In contrast, for pure metals, an amorphous phase is unstable even at extremely low temperatures, since there is essentially no barrier to crystallization. Thus, under appropriate implantation conditions, implantation-induced disorder in silicon can build up until the local free energy exceeds that of the amorphous phase. It can then be energetically favorable for the defective crystalline lattice to collapse to the amorphous phase to achieve a local minimum in free energy. Such behavior suggests that, in cases where there is some defect mobility, defect annihilation and agglomeration occurs and the amorphous phase can preferentially form at sites that minimize the local free energy. Under such situations amorphization can be considered to be nucleation limited. This nucleation limited regime is not a general case and only occurs in a limited temperature range where defects are mobile enough to form dense networks of metastable defect clusters or extended defects but the temperature is not high enough to allow such defects to evolve into defect configurations that are in thermal equilibrium to minimize the free energy.
In cases where there are no pre-existing nucleation sites for amorphization, the onset of amorphization (at elevated temperatures) usually occurs at the ion-end-of-range. Here, nucleation of the amorphous phase normally occurs where there is an interstitial excess and this corresponds roughly to the end-of-ion-range. In this regime, amorphization can exhibit interesting dependencies, including situations where the ion flux controls the critical amorphization temperature [19], as illustrated in Fig. 5. For a fixed dose of $5 \times 10^{15}$ cm$^{-2}$ for 1.5-MeV Xe ions irradiating silicon, amorphization at the end-of-ion-range can be observed only below 200°C if the average beam flux is kept below $10^{12}$ ions cm$^{-2}$ s$^{-1}$, but up to 300°C if the ion flux is raised above $10^{14}$ ions cm$^{-2}$ s$^{-1}$. This demonstrates the critical dependence of amorphization on the balance between the rate of disorder production (controlled by ion flux in the case of Fig. 5) and the extent of dynamic annealing, which is controlled by irradiation temperature. For implantation conditions on the left-hand side of the solid line in Fig. 5, no amorphous silicon was formed (only defect clusters in crystalline silicon), whereas buried amorphous layers are generated under conditions on the right. Note that the onset of amor-
amorphization in Fig. 5 fits well to an activation energy of 1.2 eV. Elliman et al. [19] noted that this value corresponds to the dissociation energy of silicon divacancies and, consequently, suggested that the stability of divacancies may control amorphization in silicon. However, more recent studies, that use other ion beams to examine the dependence of the onset of amorphization on ion flux and temperature, have shown a range of apparent activation energies between 0.5 and 1.7 eV as shown in Fig. 6, taken from the work of Goldberg et al. [22]. The conclusion is that more complex defects and defect-interaction processes may control amorphization, depending on the implant conditions used, particularly the implantation temperature.

2.4 Layer-by-Layer Amorphization

Another intriguing case of preferential amorphization is layer-by-layer amorphization, which has been observed in some cases when silicon containing pre-existing amorphous layers is reirradiated at elevated temperatures [23]. An example of such behavior is illustrated by the XTEM micrographs in Fig. 7 [24]. Clearly, the near-surface amorphous layer in Fig. 7a has increased in thickness when irradiated with 1.5-MeV Xe ions at 208°C (Fig. 7b). It
Fig. 7. XTEM images illustrating layer-by-layer amorphization of silicon by 1.5-MeV Xe ion irradiation to a dose of $5 \times 10^{15}$ cm$^{-2}$.
(a) A pre-existing surface amorphous layer on silicon prior to Xe irradiation, and (b) following Xe irradiation at 208°C. After [24]

is also interesting to note that a buried amorphous layer has also formed at the Xe end-of-ion-range under these conditions. The region between the two amorphous layers is essentially free of defects, as a result of near-perfect defect annihilation in this region. Both amorphous layers are observed to extend layer-by-layer with increasing ion dose, presumably by the preferential trapping of mobile defects at the respective amorphous/crystalline interfaces. The degree of interface smoothness may be a function of the defect mobility and trapping at the interface but could also be related to cooperative effects associated with recrystallization coherence lengths in the crystalline side of the interface.

3 Overview
of Ion-Beam-Induced Epitaxial Crystallization: Experiment and Modeling

3.1 IBIIEC Temperature Dependence

The previous section illustrated implantation conditions where amorphization by ion irradiation is nucleation limited and can give rise to preferential amorphization and layer-by-layer amorphization phenomena. If the ion-irradiation conditions are changed to enhance the rate of dynamic annealing over defect production, by raising the temperature for example, pre-existing amorphous layers can be observed to crystallize epitaxially by the IBIIEC process. IBIIEC is illustrated for the case of 1.5-MeV Xe irradiation in Fig. 8 [24]. At an irradiation temperature of 227°C, the pre-existing surface amorphous layer is observed to shrink. Increasing the dose causes further epitaxial growth of
the amorphous layer. It is interesting to note that a slight reduction in irradiation temperature to 208°C, keeping the other irradiation conditions the same, induces layer-by-layer amorphization, as previously shown in Fig. 7. If the temperature is increased further, above that corresponding to the data in Fig. 7b, the IBIEC rate speeds up. The temperature dependence of IBIEC is illustrated in Fig. 9 for the case of 600-keV Ne irradiation of silicon [25]. Note that a well-defined activation energy can be extracted from the data (0.24 eV), the magnitude of which is suggestive that defect-mediated processes control IBIEC, possibly vacancies [24, 25]. In Fig. 9, the kinetics of thermally induced epitaxial growth (SPEG) is also shown, with its activation energy of 2.8 eV [26]. It was accepted in early IBIEC studies [25, 26] that the low IBIEC activation energy arose as a result of athermal generated atomic displacements during ion irradiation. These displacements provide the defects for stimulating bonding rearrangements at the interface and hence crystallization. In the thermal (SPEG) case, the high activation energy was attributed [26] to two activation terms, nucleation of the defects influencing epitaxial crystallization and a second term involving migration and bond rearrangement. Hence, it has been suggested [25] that, in IBIEC, the first term can be eliminated by athermal defect generation and only the second activation term applies. This simple model does not take account of observations such as interface planarity and the processes involved in IBIEC may be decidedly more complex, as we discuss in later sections.

3.2 IBIEC Observations and Dependencies

Early studies [23–25, 27, 28] indicated that the IBIEC rate was proportional to ion dose and was controlled by nuclear-energy deposition. This demonstrates that atomic displacements are crucial for IBIEC. Indeed, experiments
with electron beams [29] have clearly shown that recrystallization only occurs if the energy of the electron beam is sufficient to produce atomic displacements in silicon in the region of the amorphous/crystalline interface. Several studies [23–25, 27–30] have suggested that atomic displacements generated by nuclear collisions very close to the amorphous/crystalline interface are responsible for IBIEC. For example, Fig. 10 from Williams et al. [31] shows the dependence of IBIEC on nuclear-energy deposition at the interface. In Fig. 10a, the RBS/channeling spectra show that for 1.5-MeV Ne ions at 318°C the extent of regrowth is linear with dose for this irradiation situation, where the nuclear-energy deposition is relatively constant at the interface as regrowth proceeds. In Fig. 10b, IBIEC growth is plotted as a function of nuclear-energy deposition at the interface (S_n) for Ne ion irradiation at 4 temperatures. Here, three Ne ion energies were used (0.6, 1.5 and 3 MeV) and the atomic displacements generated by the ion beam at the amorphous/crystalline interface (S_n) were obtained from simulations using the TRIM code [32]. The IBIEC rate

![Temperature Dependence of Regrowth](image)
Fig. 10. (a) RBS/channeling of Si (with a preamorphized layer) at 318°C and irradiated sequentially by 1.5-MeV Ne ions (dose increments of $3 \times 10^{10}$ cm$^{-2}$). Open circles: data for pre-existing amorphous layer. (b) IBIEC growth normalized to Ne dose $10^{16}$ cm$^{-2}$ as a function of nuclear stopping power $S_n$ (different substrate temperatures). After [31]

is observed to scale with the nuclear-energy deposition at the interface. This result strongly suggests that long-range diffusion of defects from the amorphous or crystalline sides of the interface do not contribute significantly to
IBIEC but does not rule out short-range diffusion, an issue we return to later.

The IBIEC growth rate is also found to be significantly different for different substrate orientations [28, 33, 34], where a 2–4 times slower rate is observed for (111) compared with (100) orientations. No difference between (100) and (110) orientations is observed for IBIEC. Compare this to the well-known thermally induced (SPEG) case [26], where the growth rate is 25 times slower in the (111) orientation than along (100), and 2.5 times slower along (110) than along (100). These SPEG results were accounted for by a model [2, 35] in which solid-phase epitaxial growth occurs by bond breaking and reforming processes at kinks and ledges on the amorphous/crystalline interface. Rate differences arise from the different concentrations of ledges depending on the sample orientation. Priolo et al. [36] suggested that similar processes may account for the IBIEC orientation dependence. Although it had to be corrected, this idea proved quite fruitful (see Sect. 4).

Impurity species also influence growth speeds along different orientations in thermally induced SPEG, as was discussed by Williams and Elliman [35]. The effects of impurity species on IBIEC are again qualitatively similar to those observed for thermally induced SPEG [26, 37, 38]. For example, slow-diffusing electrically active dopants, such as B and P, are observed to enhance the IBIEC growth rate [36], whereas species such as oxygen, that form strong bonds with silicon, are observed to retard the rate [39]. However, the magnitudes of the rate changes in IBIEC are considerably smaller than those observed for thermal epitaxy, again suggesting that the lower temperatures of IBIEC growth may not achieve thermal equilibrium behavior [30]. Priolo and Rimini [30] also reviewed the IBIEC behavior of fast-diffusing species such as Au and Ag, and noted the similar tendency for such impurities to strongly prefer to remain in the amorphous phase as growth proceeds. This leads to segregation at the moving amorphous/crystalline interface [40]. IBIEC allows such segregation phenomena to be studied at low temperatures, where the interface velocity can exceed the impurity diffusivity in the amorphous phase [41]. We return to this question in Sect. 4.

Although studies of the energy and depth dependence of IBIEC growth, such as that in Fig. 10, indicated that the IBIEC rate scales with nuclear-energy deposition, such scaling across widely different ion masses does not occur. Indeed, ion-mass effects were appreciated early [42], but only relatively recently have they been quantified in terms of an influence of cascade density on IBIEC rate [43]. Furthermore, a small ion-flux dependence of IBIEC [23, 42] was also found in early studies and has been examined over a wide flux range [43, 44]. Such mass effects, which illustrate the role of cascade density on IBIEC, and flux effects, which indicate the interaction times of defects contributing to IBIEC, are illustrated in Fig. 11, taken from the work of Kinomura et al. [43]. Figure 11a shows RBS/channeling spectra that illustrate the mass dependence of IBIEC. Here, 3-MeV Au, Ag, Ge and Si
ions were used to irradiate an amorphous silicon layer of about 2000 Å in thickness on a silicon (100) substrate. Different doses were chosen to provide the same total nuclear-energy deposition at the amorphous/crystalline interface and MeV ions were chosen to provide a near-constant energy deposition at the interface during IBIEC growth. It is clear from Fig. 11a that the regrown thickness increases with decreasing ion mass, even though the total nuclear-energy deposition is similar for each ion within the range of the measured depth. This clearly shows that, at the same average ion flux, the rate of nuclear-energy deposition, or the cascade density, clearly influences IBIEC. Another effect observed by Kinomura et al. [43] was a flux
dependence, whereby higher fluxes of the same ions under otherwise identical conditions resulted in less regrowth. This is again consistent with the observation that the rate of nuclear-energy deposition influences IBIEC. Figure 11b plots the IBIEC regrowth rate (normalized to constant nuclear-energy deposition at the interface) as a function of defect (i.e. vacancy) generation rate at the interface for five ion masses, four ion energies and two fluxes at 350°C. The defect generation was calculated using TRIM [32]. Note that the defect-generation rate varies over more than 4 orders of magnitude from C to Au and the normalized growth rate for C is about 4 times that of Au under these conditions. A similar dose-rate dependence for 300-keV ions has also been demonstrated by Linnros and Holmen [45] and Heera et al. [44]. However, Kinomura et al. [43] subsequently varied the ion flux for similar-mass ions over a wide range and found that cascade-density and ion-flux changes do not give identical changes to IBIEC rates. These results are shown in Fig. 12a for Au and Ag ions, where the IBIEC rate seems to vary linearly with defect generation. These data suggest that cascade size and ion flux give rise to separate influences on IBIEC rate, in addition to their common influence on defect-generation rate, as we discuss more fully below. In Fig. 12b we illustrate another case where more extensive data provide further insight into IBIEC processes. These data show that the apparent activation energy of IBIEC extracted from temperature-dependent studies can vary from 0.18 to 0.4 eV, depending on ion mass.

We discuss the significance of these observations in the discussion of IBIEC mechanisms in Sect. 3.4.

3.3 Ion-Cascade Effects on IBIEC: The Role of Atomic Displacements and Mobile Defects

A particularly important question in IBIEC is: if atomic displacements are necessary to induce crystallization, then do such displacements have to be exactly at the amorphous/crystalline interface or can they be induced away from the interface in either the crystalline or amorphous phases? It is clear from a range of early studies [25, 27, 45, 46], where the ion mass and energy were varied to change the magnitude and depth of energy deposition into atomic displacements, that atomic displacements close to the interface play the major role, but how close? Irradiation under ion-channeling conditions in the crystalline side of the interface can, in principle, help to clarify where the defects that influence IBIEC are generated, since channeling of ions along crystal lattice rows allows selective reduction in the number of atomic displacements and hence defects produced in the crystalline region. However, in the early measurements using channeling [25, 45, 46], the interpretation of the results (i.e., where the displacements that triggered IBIEC originated from) was not conclusive, mainly because it was difficult to estimate the exact number of point defects generated in the crystalline region.
after an ion beam had traversed an amorphous layer before entering the crystal. Ion-channeling irradiations using a buried amorphous layer in which to induce IBIEC were more conclusive [25, 46], since the ion beam can then be channeled in the top crystalline layer before the amorphous layer is entered, thus reducing the number of displacements in the crystal by more than 90%. A large reduction in IBIEC growth rate was observed [25, 26] for the

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**Fig. 12.** (a) Dose-rate dependence of IBIEC for 3.0-MeV Au and Ag compared with the fitting curve of Fig. 11b (solid curve). (b) Temperature dependence of IBIEC regrowth rates normalized to the number of displacements for 3.0-MeV Si, Co and Au with a dose-rate of \(2 \times 10^{12} \text{ cm}^{-2} \text{s}^{-1}\). After [43]
near-surface interface of the buried layer (40–100%), compared with a case where the ion beam was randomly oriented in the top crystal. An example of the channeling effect on IBIEC for a buried amorphous layer is shown in Fig. 13 [47]. Here, the regrowth differences are compared for channelled and random irradiations with 2-MeV C ions at 320°C in the top crystalline layer before entering a buried amorphous layer initially 1000 Å thick. Clearly, the front amorphous/crystalline interface under channeling grows only 60% of that under random alignment, whereas the rear interface appears to show no differences between the two irradiations, noting that only roughly 50% of the ion beam will be channelled in the deeper crystal region after transport through the amorphous layer. Overall, this result appears to suggest, in contradiction to earlier reports [25, 45, 46], that there is some role for mobile defects from the crystalline side of the interface rather than displacements exactly at the interface, but there remains a need for accurate simulations of displacement cascades (depth distributions of displacements) under channeling conditions before definitive conclusions can be drawn as to the precise origin of the ‘defects’ responsible for IBIEC, as we illustrate below.

Prior to reviewing cascade simulations to help interpret experimental IBIEC rates, we note a further difficulty with the IBIEC measurements under channeling conditions that were reviewed above. These measurements obtained the extent of regrowth from ex-situ RBS analysis (which has limited depth resolution) after successive irradiations. More recent studies [48] have used in-situ time-resolved reflectivity (TRR) to more accurately monitor IBIEC growth during irradiation under channeling and random alignment conditions in the silicon crystal that either overlays or underlies the amorphous layer. Results are shown in Figs. 14 and 15 for the cases of surface and buried amorphous layers, respectively. In Fig. 14, for a surface amorphous layer irradiated with 7-MeV Au ions under both random and channeling
Fig. 14. (a) Experimental reflectivity traces, as a function of dose, for 7-MeV Au ions irradiating a surface amorphous layer in silicon. The solid and dashed lines correspond to the random and channeling irradiations, respectively. (b) Depth of the interface as a function of the ion dose. (c) IBIEC rates for channeling (solid symbols) and random (open symbols) cases as a function of the interface depth. The solid line corresponds to MARLOWE calculations for the number of vacancies produced per ion per Å at the interface. After [48].

conditions, the experimental TRR traces for random (dashed line) and channeling (solid line) cases are plotted in panel (a). Note that for TRR from silicon using a 6328 Å laser, every 330 Å of growth (interface movement) corresponds to a complete oscillation between a maximum and a minimum of
the reflectivity. The comparisons between the IBIEC growth under channeling and random alignments of the Au beam are shown in panels (b) and (c) of Fig. 14. The results indicate that there is an effect of channeling in the underlying crystal but it is quite small. For example, the maximum difference in the interface depths between channeling and random alignment cases is of the order of 80 Å and the IBIEC rate for channeling implants is only 20% smaller than the rate observed for random implants.

In Fig. 15, the IBIEC results for buried amorphous layers in silicon are shown [48], again for 7-MeV Au irradiation. Panel (a) displays RBS spectra for the buried layer before irradiation (solid line) and after $3 \times 10^{15}$ Au cm$^{-2}$ random and channeling bombardments (squares and circles, respectively). Again, a clear channeling effect is observed for the front interface between channels 220–250. This difference is better quantified by an inspection of panel (b), where the position of the amorphous/crystal interfaces is plotted as a function of the ion dose. It is apparent in this figure that the deeper interface (circles) advances at the same rate ($281 \pm 10$ Å and $274 \pm 14$ Å per $10^{15}$ ions cm$^{-2}$) for channeling and random irradiations, respectively. However, the shallower interface (squares) advances much faster in random irradi-
atations than in channeling cases (262 ± 10 Å and 124 ± 5 Å per 10^{15} ions cm^{-2}, respectively).

The IBIEC growth data presented above (Figs. 14 and 15) are now compared with the results of computer simulations of collision cascades (atomic displacements). For the simulations, all displacements (point defects), both in random and channelled alignments, were calculated with the aid of the MARLOWE code [49, 50]. MARLOWE has been specifically developed for the simulation of atomic displacements in both amorphous and crystalline solids. The code is based on the binary collision approximation (BCA) [51] to construct particle trajectories. The atomic scattering is governed by screened potentials, such as ZBL [32] and Molière [52]. Thermal vibrations are simulated by a random Gaussian distribution of the lattice atoms around their equilibrium positions, with amplitude given by the Debye–Waller [53] model. Figure 16a displays the result of MARLOWE calculations for a 300-Å surface layer [48]. A reduction in the number of vacancies produced per ion per Å (η) in the crystalline region is clearly apparent, even for random bombardments. This feature can be explained as follows. Even though the nuclear-energy dissipation occurs mainly in cascades initiated by high-energy collisions between the incident Au ions and Si target atoms, the average energy transferred to a
silicon atom by 7-MeV Au ions is of the order of 0.5 keV only. Such low-energy primary Si knock-ons have a large critical angle for channeling in the crystal (of the order of several degrees) and hence the number of displacement collisions with further Si target atoms that they initiate in crystalline silicon is less than in amorphous silicon because of the high channeling probability in crystalline silicon. This explains the reduction of $\eta$ in the crystalline region, even for a random orientation of the beam. Furthermore, when the Au beam is aligned with the (100) channeling direction in the underlying crystalline silicon, the number of vacancies generated at the interface and within the crystalline region is lower than for the random case. It is also interesting to note that, under channeling conditions, $\eta$ is slightly reduced in the amorphous region, in comparison with random implants. This latter observation implies that cascades initiated in the crystalline region can produce displacements in the amorphous region, even though it is closer to the surface. A comparison of the experimentally observed $\sim$20\% lower IBIEC rate for channeling-beam alignment (Fig. 14) with the simulation data in Fig. 16a, indicates that the scale of difference between channelled and random IBIEC rates is more consistent with vacancies produced precisely at the interface than with vacancies produced in the amorphous or crystalline regions.

Figure 16b displays the results of simulations for a buried layer in silicon irradiated with 7-MeV Au ions. It is apparent that, for channeling implants, $\eta$ is strongly reduced in the crystalline region near to the surface, as one might expect. However, only a small reduction of $\eta$ is observed after the deeper interface. These features can be explained by the same arguments utilized above to explain the results for surface layers. Therefore, the most important feature displayed in Fig. 16b is that, assuming IBIEC is controlled by point defects generated at the amorphous/crystalline interface, MARLOWE predicts a large channeling effect at the front interface and a very small effect at the back interface, consistent with the experimental data for a buried amorphous layer (Fig. 15). Furthermore, the scale of the experimental IBIEC reduction rate for the front interface under channeling conditions ($\sim$50\%) appears to best correlate with the relative number of vacancies produced at the front interface (Fig. 16b), rather than displacements within the amorphous or crystalline regions, as discussed below.

The solid line in Fig. 14c corresponds to the predictions of MARLOWE for vacancies ($\gamma$) produced at the amorphous/crystalline interface. As can be readily observed, $\gamma$ drops quickly as the interface approaches the surface. This feature is a result of the reduction in the cascade density for shallow depths and the experimental IBIEC rates ($\gamma$) display a similar trend. However, $\gamma$ is clearly steeper than $\eta$ when the thickness of the amorphous layer is smaller than about 500 Å. We suggest that effects other than defect diffusion within the near-surface region could be responsible for this behavior and for the discrepancies with MARLOWE predictions. For example, it has been demonstrated previously that the IBIEC rate is affected by defect interac-
tions within individual cascades (i.e. the cascade density) as well as by defect interactions between cascades [43]. This suggests that the observed thickness dependence of $\gamma$ could be related to a distortion of the point defect profiles at the interface when the interface is close to the surface, due to cascade-density differences and cascade interactions, rather than being related to point defect diffusion. Furthermore, Kinomura et al. [54] have demonstrated that oxygen impurity atoms recoiling from the surface native oxide contribute partially to a decrease in the IBIEC rates close to the surface. Therefore, the comparison of MARLOWE predictions with the experimental results for shallow surface amorphous layers is not straightforward.

In order to more precisely determine the origin of the defects that control IBIEC, the ratio between the channeling and random IBIEC rates ($\Gamma = \gamma_c/\gamma_r$) is compared to the ratio between the corresponding simulated defect profiles. This method removes the influence of shallow surface layers, chemical contamination and cascade interaction effects that are canceled out. In Fig. 17, the ratio $\Gamma$ between the experimentally determined IBIEC rates under channeling and random conditions is compared to the ratio between the corresponding calculated defect levels ($\gamma_c/\gamma_r$) at the amorphous/crystalline
interface [48]. As can be observed, the magnitude of the experimentally determined $\Gamma$ is in good agreement with MARLOWE calculations for the ratio $\eta_c/\eta_r$. Furthermore, from the results in Figs. 14 and 15, a dominant role of defects coming from the amorphous region can be eliminated as a possibility since the simulations show that $\eta$ is reduced by only $\sim5\%$ (surface amorphous layer) or $10\%$ (buried amorphous layer) under channeling conditions, while the observed channeling effect on IBIEC is of the order of $20\%$ and $50\%$ for surface and buried layers, respectively. On the other hand, the simulations for a buried layer indicate that defects produced in the crystalline region are not likely to be participating in IBIEC, since the simulations predict a $90\%$ reduction of $\eta$ in the crystalline region close to the surface, while the observed channeling effect is of the order of $50\%$. Therefore, combining all experimental and simulation comparisons, we conclude that defects produced at or very near the amorphous/crystalline interfaces are most likely to control IBIEC. Although the precise interface defect controlling IBIEC is not revealed by these results, the data is consistent with any crystallization-enabling defect, such as a kink, produced at the interface by the ion beam.

3.4 IBIEC Models

Priolo and Rimini [30] gave an overview of various models to explain IBIEC observations up to about 1990. An early proposal suggested that annealing processes, which occur in the quenching of thermal spikes that overlap the amorphous/crystalline interface, were responsible for IBIEC [55]. Minimum free-energy arguments and differences in free energy of amorphous and crystalline silicon have also been invoked to explain the temperature dependence of ion-induced amorphization and crystallization [56]. However, such proposals do not address many of the observations and also fail to suggest which ‘defects’ may stimulate IBIEC. Vacancies were suggested by several authors [42, 57, 58] as the prime defect involved. First, the similarity of the initial activation energy of IBIEC (around 0.3 eV) to that of vacancy migration led Linmos et al. [42] to propose that migrating vacancies, produced athermally by the ion beam, mediated IBIEC, whereas, if the temperature was lowered, then the increased stability of divacancies, with a dissociation energy of 1.2 eV, may cause amorphization at the interface. This two-defect model qualitatively explains both the growth of an amorphous layer and the IBIEC process but presupposes the migration of such defects in crystalline silicon to the interface. Other defects proposed to mediate IBIEC are (charged) kinks [25, 30] and dangling bonds [59] that are formed athermally by the ion beam directly at the interface. A difficulty with a single-defect model is the fact that the apparent activation energy of IBIEC has been shown to vary from about 0.18 to 0.4 eV (see Fig. 12b). This led Kinomura et al. [43] to suggest that the rate-limiting effect in IBIEC may involve several different defect-mediated processes, depending on the cascade density at the interface and the temperature. This does not necessarily preclude kinks or other
specific interface defects as the final step in the IBIEC process, but rather suggests that more complex defect processes may be involved in the annealing of dense cascades before discrete kinks are formed. A particular concern of vacancy models is that there is now considerable weight, as was indicated through Figs. 14–17, to arguments suggesting that defects produced right at the interface dominate IBIEC.

Another explanation for both the extension of amorphous layers by ion irradiation and IBIEC is due to Jackson [20], who developed an intracascade model in which each ion penetrating through the interface creates a disordered zone. Subsequent local interaction between defects in this zone can either lead to amorphization or crystallization. The onset of either amorphization or crystallization is controlled by a rate equation in which the net rate of interface movement, \( \dot{R} \), is given by the difference between a crystallization term, \( R_{\text{c}} \), and an amorphization term, \( R_{\text{a}} \), according to:

\[
\dot{R} = \frac{dx}{d\varphi} = R_{\text{c}} - R_{\text{a}},
\]

where \( x \) is the distance of interface motion and \( \varphi \) is the ion-beam dose. The amorphization term can be written as \( R_{\text{a}} = V_{\alpha} \varphi \), where \( V_{\alpha} \) is the volume of the amorphous zone created by a single ion. Crystallization arises when defects produced by the ion beam annihilate in pairs at the interface. The simplicity of the Jackson model is attractive but it does not adequately account for ion mass and flux effects. Thus, no single existing model appears to adequately explain all observations.

### 3.5 Interface Evolution

Let us first concentrate on the properties of the interface rather than on the underlying microscopic defect mechanisms leading to the latter. As noted above, Priolo et al. [36] suggested that the kink-and-ledge mechanism [2, 35] devised to explain thermal epitaxial growth (which has since been observed directly via in-situ high-resolution TEM experiments [60]) be extended to analyze ion-beam-induced interfacial growth. In the kink-and-ledge mechanism, the interface is resolved into surfaces of minimum free energy by the formation of terraces with a \( \{111\} \) orientation, separated by \( \{110\} \) ledges so as to maximize the number of bonds with the crystal (Fig. 18). Regrowth involves thermally activated bond breaking and rearrangement at these sites, i.e., depends on the number of \( \{110\} \) ledges formed on \( \{111\} \) terraces – hence on the crystal orientation during growth. The two physical processes to consider are: (1) the probability that a kink (a dangling bond) be created at the interface along the \( \{110\} \) ledges of \( \{111\} \) terraces, where, under thermal equilibrium crystallization conditions, this quantity is essentially zero below a threshold temperature, and grows exponentially above it; (2) the change in growth speed for different orientations is due to the differences in ledge densities, but not to the number of “recrystallized” sites. The latter is constant [61]: each kink “recrystallizes” 200 atoms, the ledge structure remaining
unchanged as growth occurs and the interface roughness is very low in this case.

The extension of this model to IBIEC [62, 63] assumes that growth occurs via a similar kink-and-ledge mechanism as above, but rather than relating the growth's orientation dependence to the ledge density, Monte Carlo simulations were performed assuming that the energy deposited by the ion beam ultimately initiates dangling bonds at any site on the \{111\} terraces of the aSi/cSi interface (hence enhancing the interface roughness). The probability that a site is efficient in inducing crystallization depends on its surroundings, the most efficient ones being those that have the maximum number of neighbors on the crystal side of the interface. In this picture, the number of recrystallized sites per kink is nearer to unity than to 200, because kink propagation is limited by surface roughening, and the orientation dependence of the crystallization speed is considerably less anisotropic than that found in thermal growth. An excellent fit to the growth-orientation dependence was found by Custer et al. [62] assuming maximum roughening, i.e., no constraint on local configurational energy (Fig. 19). Note that this model – which says nothing of how the kink is created – is compatible with Jackson's model, since the latter does not consider the interface structure.

This result allows us to bridge the gap with the basic physical concepts of surface growth. How does surface roughness change as growth occurs? In most cases [64], the roughness increase with time $t$ follows scaling laws such as

$$\delta(t) \sim t^\beta,$$

where $\beta$ is an exponent that characterizes the growth mechanism. Generally, saturation sets in after a sufficiently long time $t_s$, the maximum roughness $\delta_{sat}$ then being related to the system's size $L$ via

$$\delta_{sat} \sim L^\alpha[t \gg t_s].$$
The time $t_x$ to reach saturation also depends on the system’s size according to $t_x \sim L^z$. The exponents $\alpha$, $\beta$, and $z$ characterize the growing system: $z$ is termed the dynamic exponent, while $\alpha$ and $\beta$ are, respectively, the roughness and the growth exponents. The roughness evolution may be renormalized to the system’s size [65] via the scaling law

$$\delta(L,t) \sim L^\alpha f(t/L^z),$$

with $f(u) = u^\beta$ if $u \ll 1$ and $f(u) = \text{cst}$ if $u \gg 1$,

and the exponents are connected via the scaling law $z = \alpha/\beta$. Different exponent values signal differences in the universality classes of possible surface epitaxial reconstruction mechanisms, essentially as regards the existence of spatial correlations due to surface relaxation during or after adatom deposition. In the absence of such correlations (random columnar deposition), growth is a stochastic process so that $\delta^2 \sim Dt$, where $D$ is an effective diffusion constant characterizing randomness. This leads to an exponent $\beta = 1/2$, whereas $\alpha$ is undefined since the roughness does not level off. Introducing lateral correlations due to relaxation on neighboring lower sites (“random correlated deposition”) leads to a linear [Edwards–Wilkinson [66]] equation whose exponents in dimension 1 are $\beta \sim 1/4$ for growth; relaxation-induced lateral correlations lead to roughness saturation in a finite-size system, with $\alpha \sim 1/2$. In the more realistic case where the relaxation mode generates lateral (as well as perpendicular) growth, e.g., when adatoms stick to the nearest occupied site that they find, Kardar–Parisi–Zhang (KPZ) [67] showed that a nonlinear term adds on to the Edwards–Wilkinson equation, and the expo-
ponent values are respectively $\alpha \sim 1/2$ and $\beta \sim 1/3$, with scaling $\alpha + \beta = 2$. This
universality class is particularly important in many areas of growth research, far beyond crystal surfaces. How do these results relate to ion-irradiation-induced interfacial growth? The latter's evolution does not involve any increase in the amount of matter (no adatoms), but the interface motion and roughness are modified during crystallization. This implies that matter has effectively moved along the interface. Can one specify a growth mode in terms of the theories sketched above?

In addition to assuming random initiation of growth sites on the interface, the Monte Carlo simulations of Fortuna et al. ([63] and unpublished work) included local configurational energy minimization: when a kink site was created at random, the neighboring sites – up to 3 near neighbors – were explored to identify whether they belonged (or not) to the crystal. A hierarchy of favorable growth configurations are chosen: first that where 3 neighbors belonged to the crystal, then 2, and 1.

The only free parameter is then the number of sites that the kink may “recrystallize”. Simulations were performed for a planar interface, and also for a small, (111)-faceted precipitate in order to emphasize the evolution of the interface roughness. Figure 20 shows the latter case, with (lower left, upper right) two different stages of evolution in the case where each kink only recrystallizes a single site ($n = 1$), and (lower right) a case where each kink recrystallizes up to 10 sites ($n = 10$). The two figures on the RHS correspond to the same number of runs. The effect of roughening is obvious: it is stronger and saturates more quickly when $n = 1$. Note that the rounding of the shape is solely due to kinetic growth – there is no diffusion. The growth speeds for small $n$ agree with experimental IBIEC speed values in the range where the thermal contribution to IBIEC is small, and the roughening amplitude is
Fig. 21. Early stage of (111)-plane IBIEC simulated by Monte Carlo modeling with kink-and-ledge model as described in text. LHS: $n = 10$, RHS: $n = 1$ (F. Fortuna, P. Nedellec and H. Bernas, unpublished)

...quite close to the only experimentally measured value [68]. It is interesting that the simulated values of the growth speed are in reasonable agreement with experiments. The same effect is seen in more detail on the planar interface (Fig. 21), in which the LHS shows the interface when $n = 10$ (note the triangular mounds familiar from STM studies of Si surface growth), whereas the RHS shows two stages of the roughened growth landscape obtained when $n = 1$. A logarithmic plot of the interface roughness $\delta$ as a function of the average crystallized thickness ($H$) provides the growth exponent $\beta$, shown for $n = 1$ and $n = 10$ in Fig. 22. As indicated above, the roughness exponent $\alpha$ depends on the system size (denoted here by $L$, number of atoms in a row). The lower part of the same figure shows how $\alpha$ is obtained in the two configurations. Unsurprisingly, the $n = 1$ case (no kink propagation) corresponds to the Edwards-Wilkinson universality class (random correlated deposition), whereas the $n = 10$ case, implying significant lateral growth component, fits the KPZ exponents rather nicely. The transition between the two growth modes takes place for very small values of $n$ (2, 3). Thus, we conclude that the role of the interface roughness in IBIEC is very significant, and perhaps a major one in determining the growth speed in pure silicon. When a sufficient concentration of solute atoms is involved in the IBIEC process (see
Fig. 22. (a) Evolution of interface roughness $\delta$ as a function of average crystallized height $\langle H \rangle$ from Monte Carlo simulations as described in the text. Note logarithmic scale. The growth mechanism exponent $\beta$ is deduced from the slope. LHS: case where $n = 1$, RHS: case where $n = 10$. Different curves correspond to simulations performed for different interface sizes ($L =$ number of sites). This allows (b) the roughness exponent $\alpha$ to be deduced from the size dependence of $\delta$ (E. Fortuna, P. Nedelec and H. Bernas, unpublished)

below), the interface roughness determines the precipitate density as well as the precipitation process (it is the source of Volmer-Weber growth).

As mentioned previously, these results do not bear upon the microscopic origin of IBIEC or ion-beam-induced amorphization. This was studied in detail via molecular dynamics (MD), combined in some cases with kinetic Monte Carlo simulations [69–71]. A specific, previously known structural bond defect – identified as an interstitial–vacancy (IV) pair when formed by irradiation – was able to account for many features of the amorphization process, including the latter’s temperature dependence via the IV recombination probability.
This defect is compatible with the kink structure discussed above. However, these MD simulations are still comparatively “local”, and do not yet show the interface geometry over a length scale sufficient to evaluate roughness.

4 IBIEC and Silicide Precipitation

We have seen that the crystallization mechanism for IBIEC is basically the kink-and-ledge mechanism, and that both kinetic and thermodynamic growth processes are involved. We now consider the relation between IBIEC and second-phase precipitation, which provides interesting results for interface physics where two- and three-dimensional phenomena interact strongly. Suppose we diffuse or implant metal species (such as those that easily form silicides) at per cent-range concentrations into the a-Si side of an a-Si/c-Si bilayer, and then perform IBIEC. As the interface moves through the a-Si, it crosses a solute metal “flux”; precipitation, and various phase transformations occur on the interface itself. There is a striking analogy between IBIEC and molecular beam epitaxy (MBE): the a-Si/c-Si interface, moving towards the static metal atoms in the a-Si phase, mirrors an incoming metal flux falling on the c-Si surface. The very existence of the interface motion allows us to study some dynamical properties of these transformations. Because the elementary crystallization mechanism is the same in both processes, rather general information on the building up of precipitates and phases at interfaces may be obtained by using the ion beam in the appropriate temperature range to control atomic motion at the interface. Also, such precipitates may be useful for various applications if small enough and if their structures can be controlled. Typically [72, 73], (1) Cross-sectional high-resolution electron microscopy (HREM) pictures taken at differing stages of interfacial growth showed that precipitation occurs on the crystallization front as it progresses; (2) Precipitate sizes depend on the impurity concentration – a concentration profile leads to a size distribution; (3) A detailed study [74] of FeSi₂ precipitation in Si showed that the crystallites’ structure and epitaxial relation to the c-Si host depends on their size rather than on the equilibrium phase diagram. What is the driving force for precipitation? What determines the precipitate density? What determines the phase structure? In the following, we show that interface roughness determines precipitation, hence the importance of the interfacial energy and of the strain energy in determining the phase and structure of the precipitates. These considerations are directly related to the wealth of experiments and theoretical analyses of surface-based phenomena. The consequences are interesting for precipitate size and structure engineering.
4.1 Precipitate Distribution

In MBE, surface diffusion of deposited atoms leads to island formation via atom-pair formation and growth at island ledges. In IBIEC, trapping will likely occur at "growth sites", which in the IBIEC interface are precisely those that correspond to terrace or ledge roughening. Hence, nucleation and subsequent cluster growth should occur at the "slopes" (rather than the "peaks") in the roughened interface. The average precipitate distance would replicate the average distance between these configurations. It may be deduced by analogy with the classical estimate of islanding density due to diffusion-limited growth by trapping on clusters, (in our case it is reasonable to assume volume, rather than two-dimensional, diffusion). The precipitate density $N$ is [75]

$$N \sim (D/F)^{-\gamma},$$

where $D$ is the diffusion coefficient and $F$ the number of atoms crossing the moving interface per unit surface and time. $N^{-1} \sim \langle P \rangle$, where $l$ is the distance between precipitates. Experimental values of $F$ and typical diffusion coefficient values lead to typical distances ranging from 40 to 80 nm, in quite good agreement with experiments and with the simulations shown above. Note that for concentrations in the 1–10 per cent range, this leads to Volmer–Weber-type growth and provides a form of "self-organization".

4.2 Phase Composition, Structure and Orientation

Just as in surface growth [76], the interfacial energy and strain energy terms play a crucial role in the Gibbs free energy (FE) relation as long as the surface-to-volume ratio is large. The phase compositions can be deduced from standard clustering thermodynamics (chemical-potential differences, Gibbs-Thomson growth). The formation FE of a nucleus such as that formed by roughness-induced Volmer–Weber-type growth is typically

$$\Delta G = -V\Delta G_a + A\gamma,$$

where $\Delta G_a$, is the FE difference per atom, $V$ the volume, $A$ the surface and $\gamma$, the interfacial energy. $V$ and $A$ depend on the precipitate crystal's orientation versus the substrate, and the latter in turn depends on $\gamma$. On surfaces, the resulting precipitate orientations are determined by the ratio $\gamma S/A \gamma$ ($\gamma$ differs for different orientations) where $\gamma S$ is the surface energy. At an interface, the equilibrium orientation only depends on the interfacial energy $\gamma$. After the a-Si/c-Si interface's passage, the precipitate orientation can no longer change and pseudomorphic transformations are kinetically blocked as long as the volume term above (i.e., the precipitate radius) is small enough. IBIEC thus produces "phase trapping" of structures with simple epitaxial relations to the host. Increasing the concentration, size (and surface-to-volume ratio) changes modify $\Delta G$ and the balance between the terms in the formation FE.
This effect is enhanced by the lattice strain. The total energy \( E \) of the epitaxial precipitate is a sum of the bulk total energy under hydrostatic pressure \( E_{\text{bh}} \) and of a strain-dependent term:

\[
E_0 = E_{\text{bh}} + q(c_h) \Gamma \Delta a^2,
\]

(7)

where \( q \) is a function of the crystal’s (orientation-dependent) elastic constants. \( \Gamma \) depends on bulk properties and \( \Delta a \) is the difference in lattice constants. Both terms have a parabolic dependence on the lattice constants’ change under pressure, so that an increase in the lattice strain (which adds a negative term to the formation enthalpy of the epitaxial precipitate) may drastically change the FE sequence in IBIEC-induced phase formation [74].

5 Conclusion

Qualitatively, ion-induced disorder and amorphization processes in silicon are reasonably well understood. However, the temperature dependence of defect accumulation and amorphization is quite complex, with a multitude of defect-mediated processes playing major roles depending on the irradiation temperature, ion mass, dose rate and nuclear-energy deposition along the ion track. As a result there is no overall quantitative model (with predictability) that can treat defect accumulation, defect evolution and amorphization over all temperature ranges and irradiation conditions. Available quantitative models (e.g., kinetic Monte Carlo and MD simulations) are reasonably successful at describing observations at either low temperatures (or irradiation conditions) where amorphization is favored, or high temperatures, where defect accumulation and evolution into extended defects occurs, but are only partly successful at best under conditions where both substantial dynamic defect annealing and amorphization processes are occurring together during irradiation. Similarly, there are currently different views as to the importance of specific irradiation-induced defects in the amorphization process, particularly the “growth” of amorphous layers and interface roughness, under elevated-temperature irradiation. Indeed, defect gettering to and trapping at other defects and interfaces can often control disorder accumulation and amorphization behavior but few data and models exist to describe such processes. Finally, a major unknown involves how cascade-energy density determines defect generation and residual disorder. For example, amorphization is not scalable with ion mass and flux and appears to depend in a complex manner on cascade density as well as instantaneous and average defect-generation rates.

In terms of ion-beam-induced epitaxial crystallization, there are several features of the phenomenon that are known and work well. For example, there is now strong evidence that the process is driven by atomic displacements at the amorphous/crystalline interface. The Marlowe simulation code that calculates atomic displacements for random and channeled ion irradiations can
successfully predict the effect of channeling on IBIEC growth (i.e., linear scaling of growth rate with atomic displacements at the interface) for individual ion species. The excellent agreement of simulations with experiment, suggests that individual values used in the simulations are accurate, such as nuclear-energy deposition, atomic-displacement distributions for random and aligned irradiations, as well as multiple scattering through amorphous layers and associated angular spreads.

One IBIEC observation that is not understood very well at present is the effect of cascade density on IBIEC growth rates. For example, the dependence of IBIEC growth on ion-mass has no understandable scaling and the trends are at the exact opposite to those for the ion mass dependence observed for amorphization. However, the modeling of the near-atomistic interfacial processes involved in IBIEC, associated for example with the sequence of events from initial interfacial atomic displacements, through broken bond and kink formation to “diffusional” and cooperative crystallization processes along the interface are mostly successful in explaining IBIEC observations. Finally, there are clearly a number of areas of ion-induced amorphization and IBIEC covering both observation and modeling that remain to be investigated before a complete understanding of irradiation-induced, defect-mediated processes in silicon is forthcoming.

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This book introduces materials scientists and designers, physicists and chemists to the properties of materials that can be modified by ion irradiation or implantation. These techniques can help design new materials or to test modified properties; novel applications already show that ion-beam techniques are complementary to others, yielding previously unattainable properties. Also, ion-beam interactions modify materials at the nanoscale, avoiding the often detrimental results of lithographic or chemical techniques. Here, the effects are related to better-known quasi-equilibrium thermodynamics, and the consequences to materials are discussed with concepts that are familiar to materials science. Examples addressed concern semiconductor physics, crystal and nanocluster growth, optics, magnetism, and applications to geology and biology.