

**SILICON PROCESSING
FOR
THE VLSI ERA**

**VOLUME 1:
PROCESS TECHNOLOGY
Second Editlon**

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**LATTICE PRESS
Sunset Beach, California**

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Published by:

LATTICE PRESS

Post Office Box 340
Sunset Beach, California 90742, U.S.A.

Cover design by Roy Montibon, New Archetype Publishing, Los Angeles, CA.

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Library of Congress Cataloging in Publication Data
Wolf, Stanley and Tauber, Richard N.

Silicon Processing for the VLSI Era
Volume 1: Process Technology

Includes Index
1. Integrated circuits-Very large scale integration. 2. Silicon. I. Title

ISBN 0-9616721-6-1

9 8 7 6 5 4 3 2

PRINTED IN THE UNITED STATES OF AMERICA

To my wife and life editor, Carrol Ann,
and to my children, Jennifer Laura and Stanley Charles Ross

Stanley Wolf

To my partner in life, Barbara

Richard N. Tauber

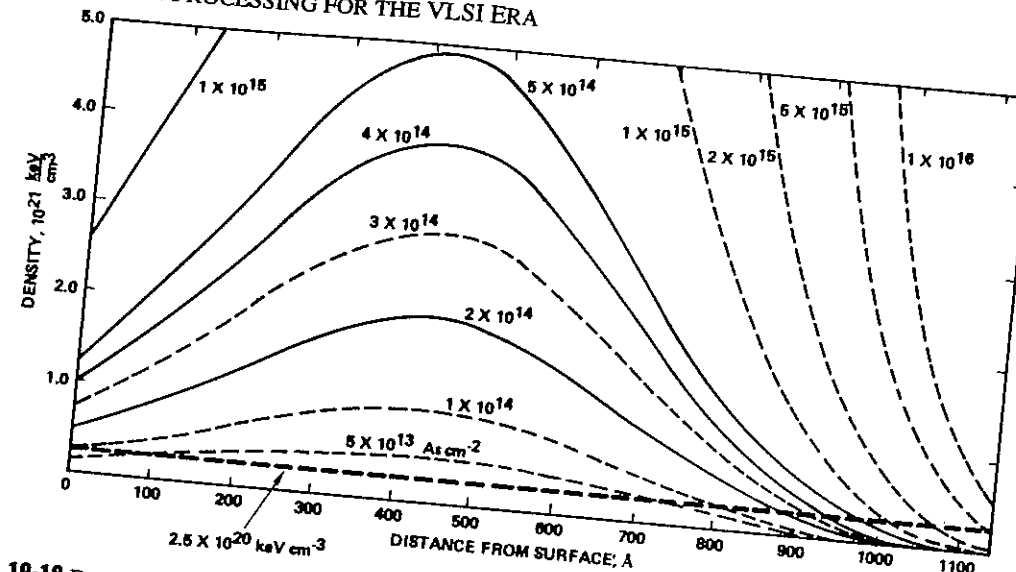


Fig. 10-18 Damage density distribution for 100-keV As implantations for doses of 5×10^{13} – 1×10^{16} As cm $^{-2}$ calculated from Brice's²⁵ curves.²⁸ Reprinted by permission of American Physical Society.

The minimum (or *threshold*) dose required to convert a crystalline material to an amorphous layer can be arrived at from a number of different viewpoints. First, it is certain that when the number of stably displaced Si atoms reaches the number of Si atoms/unit volume (e.g., 5×10^{22} cm $^{-3}$), the material has become "amorphous." When the damage density reaches this value, an amorphous condition is reached. Another view holds that there is a critical energy density that must be placed into the crystal to make it amorphous.²⁹ This critical energy E_c is given by:

$$E_c \approx f(10^{21} \text{ keV/cm}^3) \quad (10.12)$$

and the pre-factor f is 0.1–0.5 for Si. Based on this model, Brice published tables that predict the extent of the amorphous layer formation for different doses (and constant implant energy). Prussin *et al.*,²⁸ plotted the data from these tables for As implanted into Si (Fig. 10-18). A simple estimate can also be obtained by assuming that if enough energy is applied to the crystal to cause melting (for Si, 10^{21} keV/cm ^{3}); this would also produce an amorphous layer. For 100-keV As ions, the dose D_{crit} calculated from this approach (where E_0 is the beam energy in keV, and R_p in cm), is:

$$D_{\text{crit}} = [(10^{21} \text{ keV/cm}^3) R_p] / E_0 = 6 \times 10^{13} \text{ ions/cm}^2 \quad (10.13)$$

From the discussion on minimum implant dose for creating an amorphous layer, three more important aspects of amorphous layer structure can be inferred:

1. From Brice's model (Fig. 10-18), it can be seen that some implant doses will cause an amorphous layer to form below the surface of the Si, but that near the surface not enough energy has been transferred to the lattice to cause the material to become amorphous (e.g., in the case of As at 100 keV, for doses less than 1×10^{14} cm $^{-2}$, the energy density at the surface drops below the threshold required to create an amorphous layer). Thus the amorphous region does not extend all the way to the surface, but is a *buried amorphous layer*. Such buried amorphous layers have been found to exhibit profoundly different annealing characteristics than those that extend all the way to the surface.

2. In the crystalline layer just below the amorphous layer, the silicon was the recipient of impurity atoms, albeit in lower quantities than necessary to cause an amorphous region. Yet, heavy primary-crystalline-defect damage from the implanted ions exists in this zone, as well as implanted impurity atoms that must be electrically activated in order to achieve the full electrical activation of the dose. These cannot be ignored when considering an annealing strategy for amorphous layers.

3. Prussin *et al.*,²⁸ have shown that the critical energy, E_c , required to create an amorphous layer depends on the implanted species, and is 2.5×10^{20} keV/cm ^{3} , 1.0×10^{21} keV/cm ^{3} , and 5.0×10^{21} keV/cm ^{3} , for As, P, and B, respectively.

The temperature of the substrate during implantation also impacts amorphous layer formation. Figure 10-19 shows a plot of the critical dose versus reciprocal temperature for various ions.²⁸ It can be seen that for light ions such as B ^{11} , a 50°C rise above room temperature prevents the formation of an amorphous layer at any dose. This is due to the fact that B generates only a few stably displaced atoms during implantation, and a small increase in T above room temperature allows such closely spaced vacancy-interstitial pairs (Frenkel defects) to recombine.

10.3.4 Electrical Activation and Implantation Damage Annealing

In this section the methods that can be used in attempts to restore the silicon to its pre-implanted structure, and to electrically activate the implanted impurity atoms are considered. The subjects will be covered in the following order: a) electrical activation of implanted impurities; b) annealing primary crystalline defect damage; c) annealing of amorphous layers; d) dynamic annealing effects; and e) diffusion of implanted impurities.

10.3.4.1 Electrical Activation of Implanted Impurities: Since most as-implanted impurities do not occupy substitutional sites, a subsequent thermal step is employed to bring about electrical activation. The degree to which the thermal procedure is effective in electrically activating impurities is commonly determined by Hall effect measurements, but can also be checked more simply by measuring the sheet resistance, R_S .³⁰ To a first approximation, R_S is inversely proportional to the mobility μ and the implanted dose ϕ (cm $^{-2}$):

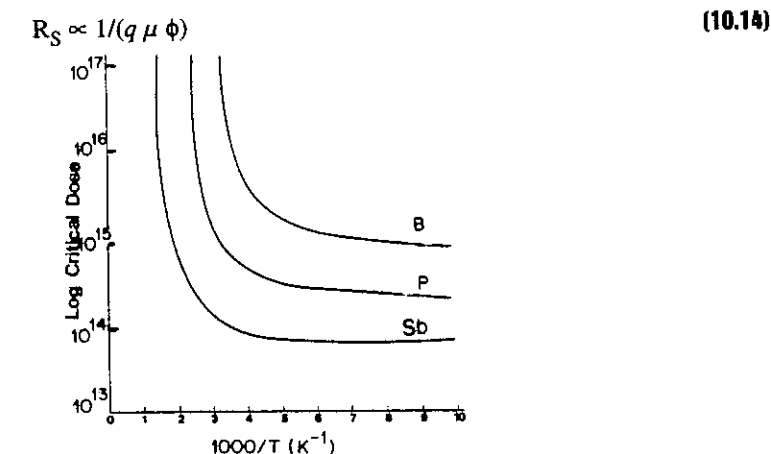


Fig. 10-19 Theoretical relationship between amorphous threshold and temperature for B ^{11} , P ^{31} , and Sb ^{121} into Si.²⁹ Reprinted with permission of Gordon and Breach Publishing Company.

where q is the electronic charge. Although μ depends strongly on the concentration of doping atoms and implantation damage, values of R_S have been tabulated utilizing known mobility data.³¹ For a known dose, full electrical activity is reached when the predicted R_S is reached.

Electrical activation of implanted impurities in amorphous layers proceeds differently than in layers with primary crystalline damage. As will be discussed, electrical activation in amorphous layers occurs as the impurities in the layer are incorporated onto lattice sites during recrystallization. Electrical activation in crystalline damaged regions exhibits more complex behavior.

For example, Fig. 10-20 shows the *isochronal* electrical activation behavior of implanted boron (i.e., anneals performed at varying temperatures, but for identical times). In this curve, the measured surface carrier concentration (normalized for different junction depths to the dose, in cm^{-2}) is used to indicate the degree of activation. That is, when $p_{\text{Hall}}/\phi = 1$, full activation is reached. Note that other impurities exhibit similar behavior to that shown in Fig. 10-20, provided the implantation does not cause a continuous amorphous layer to be formed.

The temperature range up to 500°C (Region 1 of Fig. 10-20) shows a monotonic increase in electrical activity. This is due to the removal of trapping defects and the concomitant large increase in free carrier concentration as the traps release the carriers to the valence or conduction bands. In Region 2 (500–600°C), substitutional B concentration actually decreases. This is postulated to occur as a result of the formation of dislocations at these temperatures. Some boron atoms that were already on substitutional sites are believed to precipitate on or near these dislocations. In Region 3 (>600°C), the electrical activity increases until full activation is achieved at temperatures ~800–1000°C. The higher the dose, the more disorder, and the higher the final temperature required for full activation. At such elevated temperatures, Si self-vacancies are generated. They migrate to the B precipitates, allowing boron to dissociate and fill the vacancy (i.e., a substitutional site).

Activation of implanted impurities by rapid thermal processing (RTP, see Chap. 9) has also been studied. The time-temperature cycle to reach minimum sheet resistance for As, P, and B is ~5–10 sec at 1000–1200°C, the exact condition being dependent on implanted species, energy, and dose.^{33,34}

10.3.4.2 Annealing of Primary Crystalline Damage: Isolated point defects and point defect clusters (that predominantly occur during light ion implantation), and locally amorphous zones (that are typically observed from light doses of heavy ions), are both regions of primary crystalline damage that exhibit comparable annealing behavior. At low temperatures (up to ~500°C), vacancies and self-interstitials that are in close proximity undergo recombination, thereby removing trapping defects. At higher temperatures (500–600°C), as described above, dislocations start to form, and these can capture impurity atoms. Temperatures of 900–1000°C are required to dissolve these dislocations. Note that the activation energy of impurity diffusion in Si is always smaller than that of Si self-diffusion (see Chap. 9). Therefore, the ratio of defect annihilation to the rate of impurity diffusion becomes greater as the temperature is raised. This implies that *the higher the anneal temperature the better*, with the upper limit being constrained by the maximum allowable junction depth dictated by the device design.³⁰

It is also important that the steps used to anneal implantation damage be conducted in a neutral ambient, such as Ar or N₂. That is, dislocations which form during annealing³⁵ can serve as nucleation sites for oxidation induced stacking faults (OISF, see Chap. 2) if oxidation is carried out simultaneously with the anneal (i.e., the annealing is performed in an oxygen ambient).

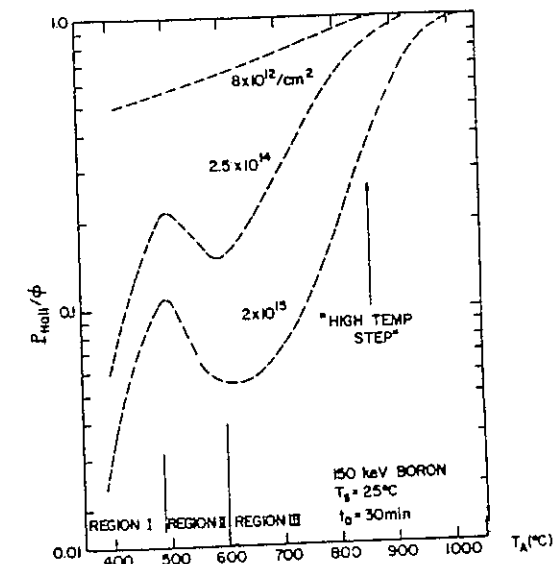


Fig. 10-20 Isochronal annealing behavior of boron. The ratio of free-carrier content, p_{Hall} , to dose ϕ is plotted against anneal temperature T_A for three doses of boron.³² Reprinted with permission of Gordon and Breach Publishing Company.

10.3.4.3 Annealing of Amorphous Layers: The annealing of continuous amorphous layers that extend to the Si surface has been found to occur by solid-phase epitaxy (SPE),³⁶ at temperatures between 500–600°C (Fig. 10-21). That is, a recrystallization process occurs on the underlying crystalline substrate, and regrowth proceeds toward the surface. The amorphous layer regrows at varying rates, depending on the annealing temperature, crystal orientation, and implanted species, although at 600°C regrowth is usually completed in a matter of minutes. Regrowth is faster on (100) than (111) Si, and impurities such as B, P, and As enhance regrowth, while O, C, N, or Ar retard regrowth. In practice, 550°C is favored, since (100) regrowth at this temperature occurs at a controllable and reproducible rate.

The impurity dopant atoms are swept into substitutional lattice sites during the SPE regrowth, and thus full electrical activation within the amorphous layer can be obtained at relatively low temperatures. The impurities that are implanted into the region beyond the amorphous layer, however, must be subjected to the higher temperatures needed to electrically activate impurities in regions of primary crystalline damage (Fig. 10-22). Therefore, to fully activate an amorphous layer, and the region of heavy primary crystalline damage behind it, higher temperature anneals than 600°C must be used (normally 800–1000°C). Note that specific *minimum* times and temperatures depend on the particular implanted species and dose.

If the amorphous layer does not extend all the way to the surface (i.e., a buried amorphous layer), the annealing proceeds differently.³⁸ That is, SPE occurs at both amorphous-single crystal interfaces, and the regrowing interfaces meet below the surface. This meeting point has been found to be a heavily damaged layer, with properties likely to cause device degradation. Thus, it is prudent to select implantation conditions that avoid the formation of buried amorphous layers. Note that if a wafer exhibits color bands after implantation and anneal, they are probably symptomatic of a subsurface damage layer left behind by a buried amorphous

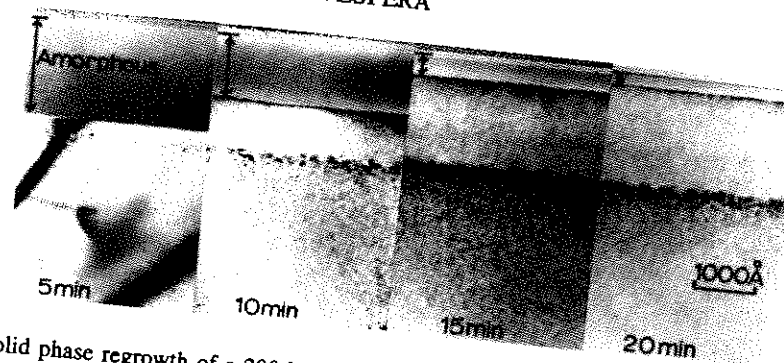


Fig. 10-21 Solid phase regrowth of a 200 keV, $6 \times 10^{15}/\text{cm}^2$ antimony implantation at 525°C. TEM cross section micrograph. Courtesy of Institute of Physics, Conference Series.³⁶

The gives rise to optical interference effects from the light reflected off the subsurface damage layers and the surface.

Some of the crystalline defects in the region beyond the amorphous layer are annealed out during subsequent thermal cycles, but others give rise to extended defects (such as dislocation loops and stacking faults), which then grow and interact. Under some implantation and annealing conditions, these defects move to the surface and eventually disappear, while in others they grow into larger structures which intersect the surface or remain in the bulk.

In a large number of cases, the total number of "excess" Si atoms found in dislocation loops after thermal annealing fits a remarkably simple model. Even though hundreds to thousands of atoms are displaced from their positions in the Si lattice by each ion impact, the number of residual Si atoms left out of the lattice after the completion of thermal annealing increases with ion dose and is closely proportional to the number of ions. This is known as the "+1" model, where the number of excess Si interstitial atoms is equal to the number of implanted dopant atoms that occupy lattice sites after thermal annealing.^{38,39} These Si interstitials arise from the dopant atom replacing the Si-atom in the lattice.

10.3.4.4 Dynamic Annealing Effects: The heating of the wafer during implantation can impact the implantation damage and the effects of subsequent annealing. A rise in temperature increases the mobility of the point defects caused by the damage, and this gives rise to healing of damage even as the implant process is occurring, hence the name *dynamic annealing*.⁴⁰ In the case of light ions, sufficient damage healing may occur to prevent the formation of amorphous layers, even at very high implantation doses. In the case of heavy ion implantations, dynamic annealing can cause amorphous layer regrowth during the implantation step.

A study by Prussin *et al.*,⁴¹ showed that the wafer cooling capability of an ion implanter can impact the structure of the damage following implantation because of dynamic annealing effects. That is, if a wafer is prevented from being significantly heated above room temperature by adequate heat sinking during implantation, dynamic annealing is minimized. On the other hand, if no heat sinking is provided and wafers are allowed to rise to temperatures ~150–300°C, dynamic annealing effects can produce changes in implantation damage structures. This typically occurs in non-reproducible and unwanted ways, such as the formation of buried amorphous layers, or crystalline layers containing high densities of dislocation loops.

10.3.4.5 Diffusion of Implanted Impurities: As described in Chap. 9, the diffusion of impurities in single-crystal Si is a complex phenomenon. The diffusion of impurities in implanted Si is

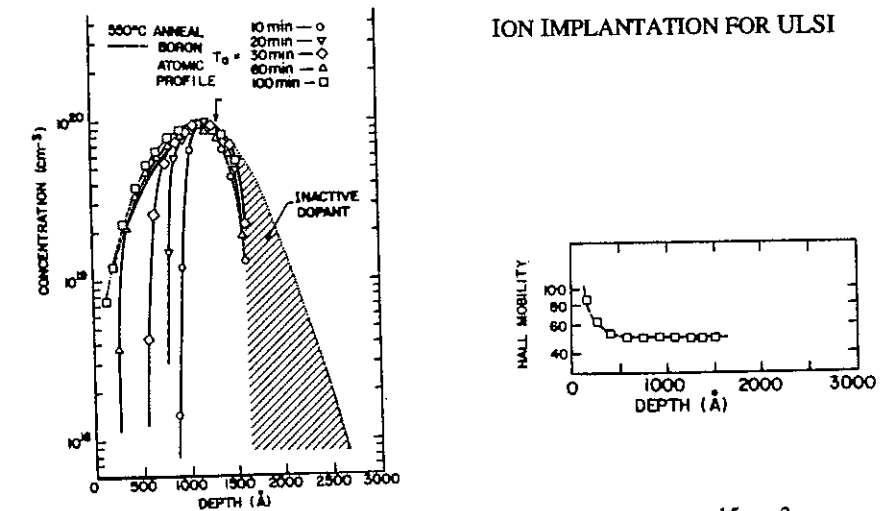


Fig. 10-22 a) Profiles for BF_2^+ implanted into $\langle 100 \rangle$ Si at 150 keV and $10^{15}/\text{cm}^2$ after different isothermal anneals. The dotted curve is the as-implanted atomic profile from SIMS analysis. The original amorphous-crystalline interface is denoted by the arrow, SPE is complete after ~100 minutes. The hatched region is electrically inactive.⁶⁴ b) Free-carrier concentration and mobility for implanted layers which illustrate dopant incorporation by solid phase epitaxy (SPE). Reprinted with permission of the American Physical Society.

even more complicated as a result of the presence of implantation damage. As an example, empirical studies of the *diffusion of B* in implanted single-crystal Si indicate that at high temperatures ($\geq 1000^\circ\text{C}$), the data appears to obey ordinary diffusion theory (Fig. 10-23). At lower temperatures, however, ordinary diffusion theory does not accurately predict the diffusion behavior. That is, at 900°C the boron profile can be closely fit only if a diffusion constant is used that is about three times the value observed under a chemical 900°C diffusion. In addition, at 700 – 800°C , the depth of profile peak remains fixed, but the concentration in the tail is much deeper than is predicted from normal boron diffusion constants. This increase in the B diffusion (by as much as 4x) in the implanted profile tail occurs during the initial stage of the thermal anneal, but slows to the equilibrium diffusion rates for the rest of the anneal. Consequently, this

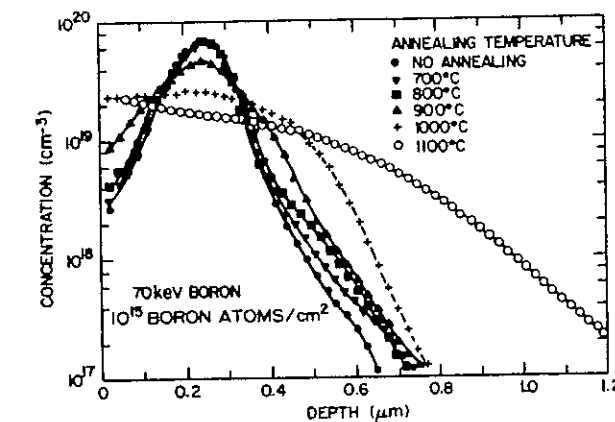


Fig. 10-23 Boron concentration as a function of annealing at various temperatures. The anneal time is 35 minutes.⁵ Reprinted with permission of Philips Research Reports.