Ion implantation and “Defect Engineering”

most important process of doping in Si planar technology

**Advantages:**
- fast, homogenous on large wafers, reproducible result
- exact control of implanted amount of dopant (measurement of current); especially important for small dopant levels
- excellent cleaning of dopants during implantation by mass separation
- simple mask techniques with thick oxide-, nitride- und photo lacquer layers
- doping through thin passivation layers
- doping profile easily adjustable by multiple implantation (not possible by diffusion techniques)
- very small device structures possible

**Disadvantages:**
- irradiation damage up to amorphisation
- additional annealing steps necessary (defect annealing)
- doping atoms often not at regular lattice sites after implantation (interstitial position); electrical activation necessary by additional annealing (diffusion of dopants, danger of impurities)
- implantation only possible for near-surface region
- Channeling leads to larger penetration depth of a fraction of dopant atoms
Some historical remarks about ion implantation

1952: bombardment of diods with He - improvement of blocking behavior (Ohl)
1955: attempt to dope Ge failed due to implantation defects (Cussins)
1957: first patent for ion implantation technique includes annealing step (Shockley)
1962: radiation detectors made by P-implanted Si
1963: Lindhardt, Scharff und Schiøtt – LSS theory for ion penetration in solids
1963: experimental study of ion implantation in crystalline and amorphous solids
1965: breakthrough by many studies

Increasing interest due to high technological importance
LSS-Theory

- LSS-Theory: interaction of ions with amorphous solids (1963: Lindhardt, Scharff und Schiøtt)
- no channeling effect considered (amorphous state), no diffusion and no defect interaction
- interaction mainly by elastic collisions with cores and inelastic interaction with electrons
- energy loss cross section (Bremsquerschnitt) $S$

\[
S_{e,n} = -\frac{1}{N} \left[ \frac{dE}{dz} \right]_{e,n}
\]

$N$ ... atomic density
$z$ ... distance

for B in Si: $E_1=3$, $E_2=17$ and $E_3=1000$ keV
for As in Si: $E_1=73$, $E_2=800$ and $E_3=10^5$ keV
Interaction of ions with solids

- elastic interaction: classical scattering theory is a good approximation
- it is obtained by energy and momentum conservation during central impact:

$$T_m = 4 \frac{m_1 m_2}{(m_1 + m_2)^2} E$$

$T_m$ is maximum transferable energy during central stroke
- $T_m$ becomes maximum for equal masses ($T_m = E$)
- electronic deceleration is function of ion energy
- it is possible by this theory to calculate implantation depth distributions
Implantation depth distributions of ions

\[ N(x) = \frac{N_0}{\sqrt{2\pi \Delta R_P}} \exp \left[ -\frac{(x - R_P)^2}{2\Delta R_P^2} \right] \]

- maximum doping is

\[ N_{max} = \frac{N_0}{\sqrt{2\pi \Delta R_P}} \]

- \( R_P \) ... projected range of implanted ion
- \( N_0 \) ... implanted dose
Implantation-induced defect generation

- when transferred energy > **displacement energy** (10 - 40 eV):
- **Frenkel pairs** are generated as result of a displacement cascade
- vacancy only stable, when it is located outside of recombination volume of interstitial atom (size of this volume is temperature dependent)
- primary ion generates many vacancies, but only a few survive
Depth distribution of atomic displacements

- Electrons (e.g. 1 MeV) generate in Si just one Frenkel pair (bad energy transfer due to very different masses)

\[ T_m = 4 \frac{m_1 m_2}{(m_1 + m_2)^2} E \]

- Ions transfer much more energy → generation of defect cascades
- Sub-cascades appear
- Heave ions: deposited energy density is larger, implantation depth smaller
- Implantation damage = f (mass ratio Ion/target atom; energy; dose; dose rate; temperature)

\[ m_{\text{Ion}} < m_{\text{Target}} \]

- e.g. B in Si

\[ m_{\text{Ion}} > m_{\text{Target}} \]

- e.g. As in Si
Depth distribution of atomic displacements

- Depth distribution of defects can be determined by Monte-Carlo-methods.
- TRIM: TRansport of Ions in Matter (DOS)
- SRIM: Stopping and Range of Ions in Matter (Windows)
- Does not take into account defect annealing, diffusion, dose rate effects and channeling
- Defect concentration too large, but distribution can sufficiently be calculated
- Maximum of defect density before maximum of implanted ions
Depth distribution of atomic displacements

- SRIM is rather rough due to many simplifications
- however, comparison with more sophisticated simulations and experiments shows no strong deviations
- more difficult: simulations for ion implantation in compound semiconductors (e.g. InP)
- there are simulation programs which take into account the defect interaction and the crystal structure (e.g. Crystal-TRIM)
Defect evolution according to Hecking

- Coexistence of crystalline and amorphous phases; relative fraction changes with implantation dose
- Range I – weak damage: defect density increases continuously
- Range II – medium damage: equilibrium between defect generation and annihilation of defects
- Range III – strong damage: collapse-like amorphization during further accumulation of defects (depend on dose and dose rate!)
Amorphization dose is function of temperature and dose rate

- most simple assumption for calculation of amorphization dose: all target atoms must be moved ones
- however, real dose is even larger due to defect annealing during implantation
- no amorphization for B implantation in Si for $T > 300K$ due to defect interaction and annealing

\[
\text{amorphization dose} = f(T)
\]

influence of dose rate on defect generation
Channeling effect

- Ions penetrate deep along low-index axis into the crystal → channeling effect
- penetration depth can be 10 times larger compared to a „random“ direction
- in case of amorphous oxide cap layer: ions will be scattered, only a few will “find” the channels
- in semiconductor technology: tilt angle 7°... 10° to avoid channeling

Channeling effect during tilt for a 450keV-P-implantation in Si <111>

dependence of channeling effect on oxide coverage for 300 keV P ions
Defect generation in Si during weak damage

- defect density is function of dose: $[\text{defect}] \propto \Phi^{0.5}$
- exception: Si into Si, because implanted Si-ions are built-in on lattice site immediately: $[\text{Si}_V]$ smaller
- e.g. boron ends at interstitial position, needs additional annealing to be $B_{\text{Si}}$

Change of material properties by ion implantation

- many material properties change during implantation
- decrease of minority carrier lifetime: \(10^{12} \text{ cm}^{-2} \text{ B in Si} \rightarrow \tau = 10^{-9} \text{ s}\)
- free charge carriers are compensated; \(\rho = 10^6 \ldots 10^9 \Omega \text{ cm}\) obtainable
- carrier mobility decreases too; may become smaller than 1 cm\(^2\)/Vs (normal >10\(^3\))
- optical transmission becomes smaller by additional energy levels in the band gap
- refraction index (Brechungsindex) changes (thus also reflection index): light propagates in an inner layer (integrated light pipe)
- SIMOX: hidden SiO\(_2\) isolation layer can be done by oxygen implantation and annealing
- for high doses: density- and volume change
- change of elastic and plastic properties (embrittlement of reaction pressure vessel steel in nuclear power plants)

Detection of defect density by observation of reflection coefficient; depth information obtained by layer-by-layer removal
Defect detection by RBS (Rutherford Backscattering)
Defects after ion implantation

Amorphization by ion implantation and subsequent defect annealing can easily be studied by RBS.

- Elastic scattering from surface provides maximum energy of observed ions.
- Is not equal to maximum energy of probe ion (often H\(^+\) or He\(^+\)) due to collision law.
Annealing of implantation defects

- implantation-induced defects must be annealed; for Si at 900° to 1000°C (often by infrared light as „rapid thermal annealing“ - RTA)

- amorphous layers may have very good crystalline properties after annealing treatment
- high defect density can easily be measured by Rutherford-backscattering during annealing treatment
Annealing of implantation defects in Si

below RT: monovacancies and interstitials
200 - 300 K: clustering of vacancies (formation of divacancies); formation of dislocation rings
400 - 500 K: E-center annealing (dopant atom-vacancy-complex) of group V atoms
around 500 K: E-centers of group III atoms
around 550 K: divacancies
600 - 1000 K: epitaxial recrystallization of amorphous layers (from crystalline side)
>1200 K: dislocation loops
1683 K: melting point
• Positron Annihilation is very sensitive for detection of open-volume defects
• main annealing stage at 750 K (vacancies, divacancies and E-centers are annealed before)
• different annealing behavior for Cz-Si (contains up to $10^{18} \text{ cm}^{-3}$ oxygen)
• obviously oxygen is part of defect complex in Cz-Si
Defect reactions during annealing

- during annealing: defect reactions take place
- so-called “S-W-Plot” of positron annihilation shows a sequence of different open-volume defects
- behavior in Cz-Si rather complicated: defect complexes are formed and dissolved during heating
Oxygen-vacancy-complexes in Cz-Si

- Infrared absorption of electron irradiated Cz-Si during annealing (Ikari, 1995)
- VO = so-called A-center anneals at RT
- many different $V_xO_y$ complexes are formed in a sequence
Defect reaction during annealing

- Implantation leads first to supersaturation (Übersättigung) of atoms on interstitial positions
- simple reaction to diminish the distortion energy: formation of dislocation loops during annealing
- annealing at 800°C: diameter ca. 20nm, density 300 ... 650 µm⁻²
- further annealing leads to larger dislocation structures

Fig. 6.19 Interstitielle Versetzungsschleifen in Silicium, das mit 2 × 10¹⁶ cm⁻² Arsen bei 40 keV durch 10 nm SiO₂ implantiert und bei 970°C für 30 min ausgeheilt wurde [456]
implanted dopant atoms are not electrically active after implantation, e.g. B is not immediately active as an acceptor
reason: dopant atoms are first on interstitial positions
there they do not act as shallow dopant
moreover: occupation of defect levels in band gap lead to compensation of carriers
to reduce both effects: annealing
activation of carriers for B:Si at about 600 K, is temperature of divacancy annealing
Gettering of impurities

- most important ways of gettering:
  - capture by lattice defects
  - decrease of diffusivity by forming chemical bounds
- irradiated Si layer getters rather good
- Example: $10^{16} \text{ cm}^{-2} 100 \text{ keV-Si-Ionen}$ in Si
- getter experiments show that Cu and Ni getters easily, but Fe, Co and Au only slowly
- Differences due to solubility and diffusion
- result: Ar-radiation damage getters better than P-implantation at $T<1000^\circ\text{C}$

backscattering spectra (2 MeV He-Ions); radiation damage from front side, and Ni in-diffusion from back side
Problem: sputtering of material by ion implantation

- ions are also used to remove surface layers: sputtering (cleaning; depth profiles for chemical analysis with SIMS or AES)
- mostly no direct process
- energy deposited under surface leads to emission of atoms from surface

<table>
<thead>
<tr>
<th>Ion</th>
<th>$10^{15}$ Dosis (cm$^{-2}$)</th>
<th>$10^{16}$</th>
<th>$10^{17}$</th>
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<tbody>
<tr>
<td>B</td>
<td>$6 \times 10^{-2}$ nm</td>
<td>0,6 nm</td>
<td>6 nm</td>
</tr>
<tr>
<td>Ar</td>
<td>0,35 nm</td>
<td>3,5 nm</td>
<td>35 nm</td>
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<tr>
<td>As</td>
<td>0,6 nm</td>
<td>6 nm</td>
<td>60 nm</td>
</tr>
<tr>
<td>Sb</td>
<td>0,78 nm</td>
<td>7,8 nm</td>
<td>78 nm</td>
</tr>
</tbody>
</table>
Problem: diffusion during annealing

- dopant atoms may diffuse during annealing of implantation-induced defects
- also during activation and defect annealing
- diffusivity is increased due to radiation damage

- $R_p$ is expected depth of implantation
- defect-enhanced diffusion during 750°C-annealing
Problem: diffusion during annealing

- proton irradiation provides sharp defect peak (depth is controlled by energy)
- shows clearly defect-induced diffusion
- experiment: diffusion in As:Si
- As is found in large depth, when proton irradiation creates defects in such a depth
- when defect depth is too large: effect disappears

Literature about ion implantation:
- Ryssel/Ruge: „Ionenimplantation“, Teubner 1978

Strahlungsbeschleunigte Diffusion von Arsen in Silicium durch Protonenbeschluß bei 900°C für 10 min abhängig vom Ort der Leerstellengeneration, der durch einen Pfeil gekennzeichnet ist
Application: Ion-cutting and wafer bonding of GaN-Wafers

- proton irradiation creates defect-rich zone
- thin layers of GaN can be put on any substrate
- one wafer can be used to produce many layers

H Implantation (high dose)

- H rich zone
- WBG

Host substrate

Wafer-Bonding

Recyclable wafer

New heterostructure

Splitting

Ion-Cut Process

~550°C

(current research of MPI Halle 2007: Dr. O. Moutanabbir)
Objective:

In order to draw a precise mechanistic picture of H-induced splitting of WBG materials a deep investigation thermal evolution of H-defect complexes is required.

Example:

H-induced splitting of free standing GaN:

As-implanted GaN: $2.6 \times 10^{17} \text{ H}^+ / \text{cm}^2$ at 50 keV

High magnification XTEM image showing nanovoids (or nanobubbles) which appear bright.

Splitting at 600 °C