2. Point Defects

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(F-center in NaCl)
2.7 Vacancies in thermodynamic equilibrium

statistical considerations

• change of free enthalpy during formation of $N_V$ Schottky-type vacancies ($N$ .. number of atoms; $W_V$ .. vacancy formation energy)

$$\Delta F = N_V \cdot W_V - T \Delta S_V$$ (positive energy term can be compensated by gain of entropy)

$\Delta S_V$ is complete entropy gain; is calculated in the following

probability to form $N_V$ vacancies in $N$ atoms is equal to probability to choose $N_V$ atoms out of $N$ atoms (numerator):

$$G = \frac{N(N-1) \cdots (N-N_V+1)}{N_V!} = \frac{N!}{(N-N_V)!N_V!}$$

The factor $N_V!$ in the denominator excludes those cases which differ only by the different order of pick-out of atoms.

using the Boltzmann-Equation and the Stirling approximation:

$$\Delta S_V = k_B \cdot \ln G = k_B \ln \frac{N!}{(N-N_V)!N_V!}$$

$\ln x! \equiv x \ln x - x$
2.7 Vacancies in thermodynamic equilibrium

it follows:

$$\Delta S_V = k_B \left[ N \ln N - (N - N_V) \ln(N - N_V) - N_V \ln N_V \right]$$

in thermal equilibrium: $\Delta F$ is extreme value

$$\left( \frac{\partial \Delta F}{\partial N_V} \right)_T = W_V - k_B T \ln \frac{N - N_V}{N_V} = 0$$

$$\ln \frac{N_V}{N - N_V} = - \frac{W_V}{k_B T}$$

in the lattice: $N_V \ll N$ \hspace{1em} (in real crystal $N/N_V > 10^3$)

$$N_V = N \cdot \exp \left( - \frac{W_V}{k_B T} \right) \quad [1]$$

• thus: vacancies must exist in an ideal crystal at $T > 0$ !
2.7 Vacancies in thermodynamic equilibrium

- example: $T=1000K$ and $W_V = 1 \text{ eV} \Rightarrow N_V/N \times 10^{-5}$
  $T=1000K$ and $W_V = 3 \text{ eV} \Rightarrow N_V/N \times 10^{-15}$
  not detectable

- real example: vacancies in Au $W_V = 0.98 \text{ eV}$, but in Si $W_V > 3.6 \text{ eV}$
- vacancy concentration is slightly larger compared to Eq. [1]
- further factors to be taken into account:
  - interaction of vacancies
  - influence of point defects to $\Delta S$
  - volume work for dilatation of lattice
- defect density often much larger: crystal far from thermal equilibrium
- excess vacancies due to e.g. irradiation by fast particles
- also: vacancies can be quenched-in by very fast quenching
- quenching rate must be about $10^4 \text{ s}^{-1}$, then a large fraction of thermal vacancies remain
- during slow warming-up: vacancies become mobile (migration energy required)
experimental results

- positron annihilation detects vacancies in thermal equilibrium
- increase of peak height $H/H_0$ of angular correlation is due to increasing number of vacancies
- slope of Arrhenius plot gives vacancy formation enthalpy $H$ ($H=U+pV$)
- only possible in metals
- in semiconductors: $H$ is too large, so number of thermal vacancies is too small to be detected
2.8 Irradiation-induced point defects

2.8.1 Generation of defects

- generation often done by **electron irradiation**
- displacement energy in metals and semiconductors is about 10 ... 30 eV
- electron threshold energy still about 500 keV
- reason: only a small fraction of electron energy can be transferred to atom (collision law)
- maximum transfer during central collision:

\[
T_m = \frac{4m_1 m_2}{(m_1 + m_2)^2} \cdot E_{\text{incident}} \quad [2]
\]

- example: \(m_1 = m_e = 9.1 \times 10^{-31} \text{ kg}\); \(m_2 = m_{\text{Cu}} = 1.06 \times 10^{-25} \text{ kg}\)
  \(\Rightarrow T_m = 4m_e/m_{\text{Cu}} \times E_{\text{incident}} = 8.6 \times 10^{-6} \times E_{\text{incident}}\)
  (some relativistic corrections are required)
- using electrons up to several MeV, mostly Frenkel pairs are generated
2.8.1 Generation of defects

- **Ion implantation** is most important doping method in semiconductor technology
- mass $m_1$ and $m_2$ in Eq. 2 are comparable (situation like billiard balls)
- however: penetration depth for ions of 100 keV is about 1 μm (1 MeV electrons $>$ 0.5mm)
- ions produce extended defect cascades; energy large enough for $10^4$ displacement events
- however: only a few defects survive (stationary state reached after 1 ps)
- also larger point defect clusters are generated

![Computer-simulated defect cascade in {100} plane of Cu. $T=250$ eV, $t_a = 0.06$ ps, $t_b = 0.35$ ps, $t_c = 1.5$ ps. Stationary result after 1.5 ps: 5 vacancies and 5 interstitials.](image)

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ion implantation

• important dopant species in Si are As and B
• in order to obtain homogenous doping depth profiles: multiple implantation steps with different energy

![Graphs showing depth distribution of implanted B (As) atoms in silicon and depth distribution of displaced atoms in B-implanted Si.]

• when implantation dose large enough: lattice becomes amorphous
• amorphisation dose is function of ion mass, target species, and temperature
2.8 Irradiation-induced point defects

- temperature dependence of amorphisation dose is strong
- at elevated temperature: defects anneal during irradiation
- at room temperature: boron implantation will not lead to amorphisation
- in technology: defects must be annealed
- often: rapid thermal annealing (RTA)
- in Si: 30s at 950°C
- done by light illumination by strong halogen lamps (few kW)

Temperature dependence of amorphisation dose for different ions in Si
Rutherford Backscattering

- classical method to investigate ion implantation defects: Rutherford Backscattering

- probe atoms (H, He) penetrate into the sample into low-index directions (channels)
- defects which are present scatter the probe atoms and raise the backscattered intensity
- defect depth profiles can be determined
2.8.2 Annealing of excess point defects

- irradiation defects far from thermal equilibrium but still stable (frozen-in)
- increasing temperature: defects start migration

\[ N = N_0 \cdot \exp \left( -\frac{E_m}{k_B T} \right) \]

\( E_m \) ... migration energy

- electrical residual resistance at low temperature: sensitive for defects (electrons are scattered during movement in electric field)
Annealing of excess point defects

- annealing starts at very low temperatures (in metals: interstitials have smallest migration energy)
- many annealing stages; during annealing: defect reaction (e.g. formation of vacancy clusters)
- often: several mechanisms lead to disappearance of same defect: vacancies vanish due to migration of interstitials and vacancies itself
- several stages (A-E) for interstitials: close Frenkel pairs (A-C) and separated interstitials (D+E)
- curve b: electron irradiation
  curve k: plastic deformation
  curve a: quenched sample
- stage I + II: interstitial annealing
- stage III: vacancy annealing

Isochronal annealing curve of Cu after 3-MeV-electron irradiation ($T_{\text{irr}} = 4.5$ K)
Annealing of excess point defects

- example: defects after electron irradiation in Ge ($E_{e-}=2$ MeV, $T_{irr}=4K$)
- distinct annealing stage at 200K
- sample with highest dose: formation of divacancies during annealing (they anneal at about 400K)
- formation of divacancies prove: it is no movement of interstitial but vacancies
- this is supported by the fact that the vacancies disappear completely in this stage; interstitial stage always incomplete

(Polity et al., 1997)
Defect reactions

- defect reactions during annealing sequence is usual effect
- they could be rather complex
- typical example: defect annealing in Cz-Si after low-temperature electron irradiation
- many different oxygen-vacancy complexes are formed
- most simple defect is the so-called A-center
- during annealing: sequence of different $V_xO_y$ complexes are formed
- defects stable up to 800°C, although a monovacancy anneals at about 200K
- oxygen stabilizes the defects

V-O complex (A-center)
2.9 Aspects of defect chemistry

- chemical or defect reaction: \( v_A \cdot A + v_B \cdot B \rightleftharpoons v_C \cdot C + v_D \cdot D \)  
  \( v \ldots \) number of moles

  reaction index: \( \lambda = \frac{v_C + v_D}{\sum v_i} \)

- prior to reaction: \( \lambda = 0 \); complete reaction \( \lambda = 1 \)
- in thermodynamic equilibrium: \( 0 < \lambda < 1 \)

- equilibrium condition:
  \[ \left. \frac{\partial G}{\partial \lambda} \right|_{T,p} = 0 \]  
  minimum of free enthalpy

- reaction runs spontaneously only when:
  \[ \left. \frac{\partial G}{\partial \lambda} \right|_{T,p} < 0 \]
The mass action law

- chemical or defect reaction \( A + B \xrightleftharpoons[k_1]{k_2} C + D \) 
  \( k_1 \) ... reaction velocity coefficients \( c_i \) ... concentrations

\[
\frac{dc_A}{dt} = \frac{dc_B}{dt} = -k_1 \cdot c_A \cdot c_B \quad \text{and for return reaction:} \quad \frac{dc_C}{dt} = \frac{dc_D}{dt} = -k_2 \cdot c_C \cdot c_D
\]

- in case of thermodynamic equilibrium: velocity in both directions identical

\[
\frac{dc_A}{dt} = \frac{dc_C}{dt} \quad \text{and thus:} \quad \frac{\bar{c}_C \cdot \bar{c}_D}{\bar{c}_A \cdot \bar{c}_B} = \frac{k_1}{k_2} = k \\
\bar{c}_i \quad \text{... concentration in equilibrium}
\]

- equation is called **mass action law**

- not only for chemical reactions: intrinsic conductivity in semiconductors

\[
0 \xrightleftharpoons{n + p} \quad \text{mass action law:} \quad \frac{n \cdot p}{N} = k \\
\text{N ... number of all electrons}
\]

and thus: \( n \cdot p = k' \)
Defect chemistry in HgCdTe

- HgCdTe is used as infrared detector; dominating defect is $V_{\text{Hg}}^{2-}$ (twofold ionized acceptor)
- vacancies are in equilibrium with vapour $p_{\text{Hg}}$ over crystal

$$e^{-} + h^{+} \leftrightarrow 0$$

$$V_{\text{Hg}}^{2-} + 2h^{+} + Hg(gas) \leftrightarrow Hg_{\text{Hg}}$$

- electrical conductivity is sum of intrinsic conduction and ionization of $V_{\text{Hg}}$ acceptors

- mass action law:

$$n \cdot h = k_i$$

$$[V_{\text{Hg}}^{2-}] \cdot h^2 \cdot p_{\text{Hg}} = k_v$$

- neutrality condition:

$$n - h + 2 \cdot [V_{\text{Hg}}^{2-}] = 0$$

intrinsic part $n = h$ (at high temperatures)

extrinsic part $2 \cdot [V_{\text{Hg}}^{2-}] = h$ (3)

- technical use at $T < 100K$ (no intrinsic conduction); combination of (1) to (3) gives:

$$h^3_{77K} - \frac{k_i^2 \cdot p_{\text{Hg}}}{2k_v} h^2_{77K} + 2k_i h_{77K} - \frac{2k_v}{p_{\text{Hg}}} = 0$$

(4)
Defect chemistry in HgCdTe

\[ h_{77K}^3 - \frac{k_i^2 \cdot p_{Hg}}{2k_v} h_{77K}^2 + 2k_i h_{77K} - \frac{2k_v}{p_{Hg}} = 0 \]  \hspace{1cm} (4)

- is equation which defines connection between Hg partial pressure and concentration of Hg vacancies in crystal (because of \( h_{77K} = 2 [V_{Hg}] \))
- constants \( k_i \) and \( k_v \) were determined by electrical measurements (Hall effect)
- lines in figure: result of simulation by eq. (4); measured points: experimental data of Hg vacancy concentration obtained by positron annihilation

Density of mercury vacancies in Hg\(_{0.8}\)Cd\(_{0.2}\)Te (Krause-Rehberg et al. 1995a) as determined by positron lifetime spectroscopy (symbols). The vacancy densities were adjusted within the region of existence (dotted line) of the compound during post-growth annealing in a two-zone furnace at the given Hg vapor pressure and the indicated sample temperature. The full lines are the isotherms calculated according to (6.5) from the Hall effect measurements of Vydyanath (1981).
Defect chemistry

- treatment of quasi-ternary compounds becomes rather difficult
- very large number of intrinsic defects
- but in special regions: only a few defects dominate
- calculation of the dominating defects requires the knowledge of thermodynamic constants which are usually only roughly known
- diagram only valid for a constant temperature

CuInSe₂

Majority defects depicted in a ternary diagram of Cu, In, and Se for larger deviations from ideal stoichiometry. There are four regions characterized by the dominating defects: (1) Cu₂⁺, Cu₂⁻, (2) V₂⁺, In₂⁻, Cu₂⁻, (3) In²⁺, V⁻, and (4) In₂⁺, V₂⁻, V⁻. The composition range bounded by solid lines shows n-type conductivity.