

ISOLDE Workshop and Users Meeting 2009

Uncovering New Diffusion Phenomena in Compound Semiconductors

Th. Wichert¹, J.Kronenberg¹, K. Johnston¹, J. Cieslak¹, M. Deicher¹, F. Wagner¹, H. Wolf¹, and The ISOLDE collaboration²

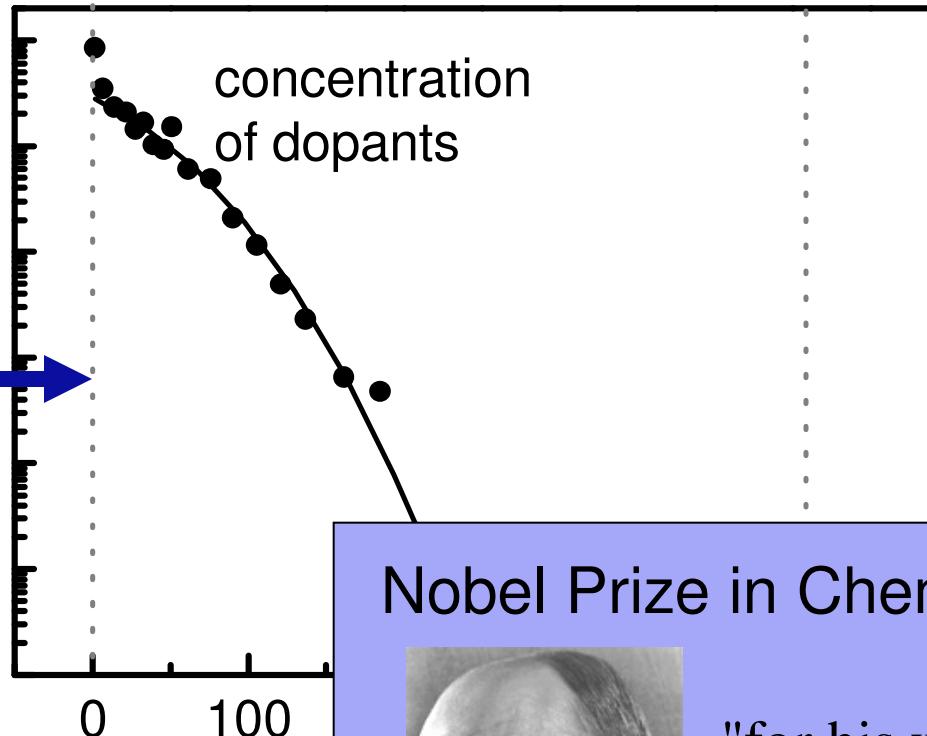
¹*Technische Physik, Universität des Saarlandes, D-66123 Saarbrücken, Germany*

²*CERN, CH-1211 Geneva 23, Switzerland*
thw@tech-phys.uni-sb.de

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Diffusion in Solids

one-sided
source



Nobel Prize in Chemistry 1943



"for his work on the use of isotopes as tracers in the study of chemical processes"



George de Hevesy

Fick's First Law

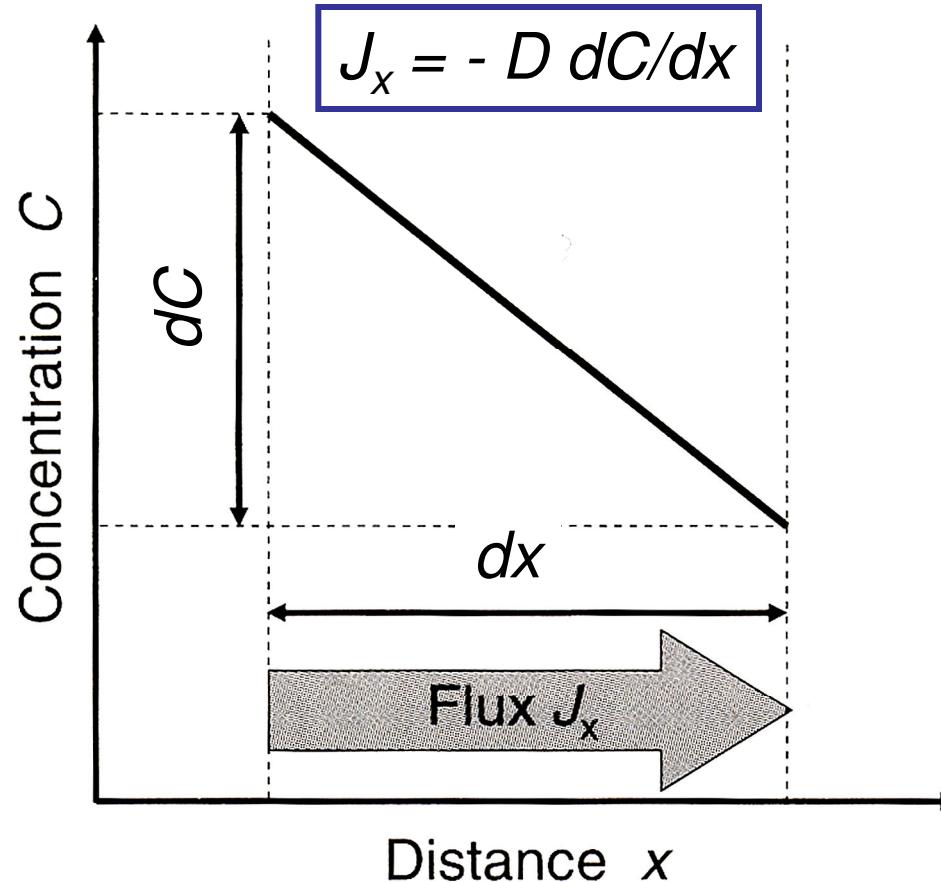
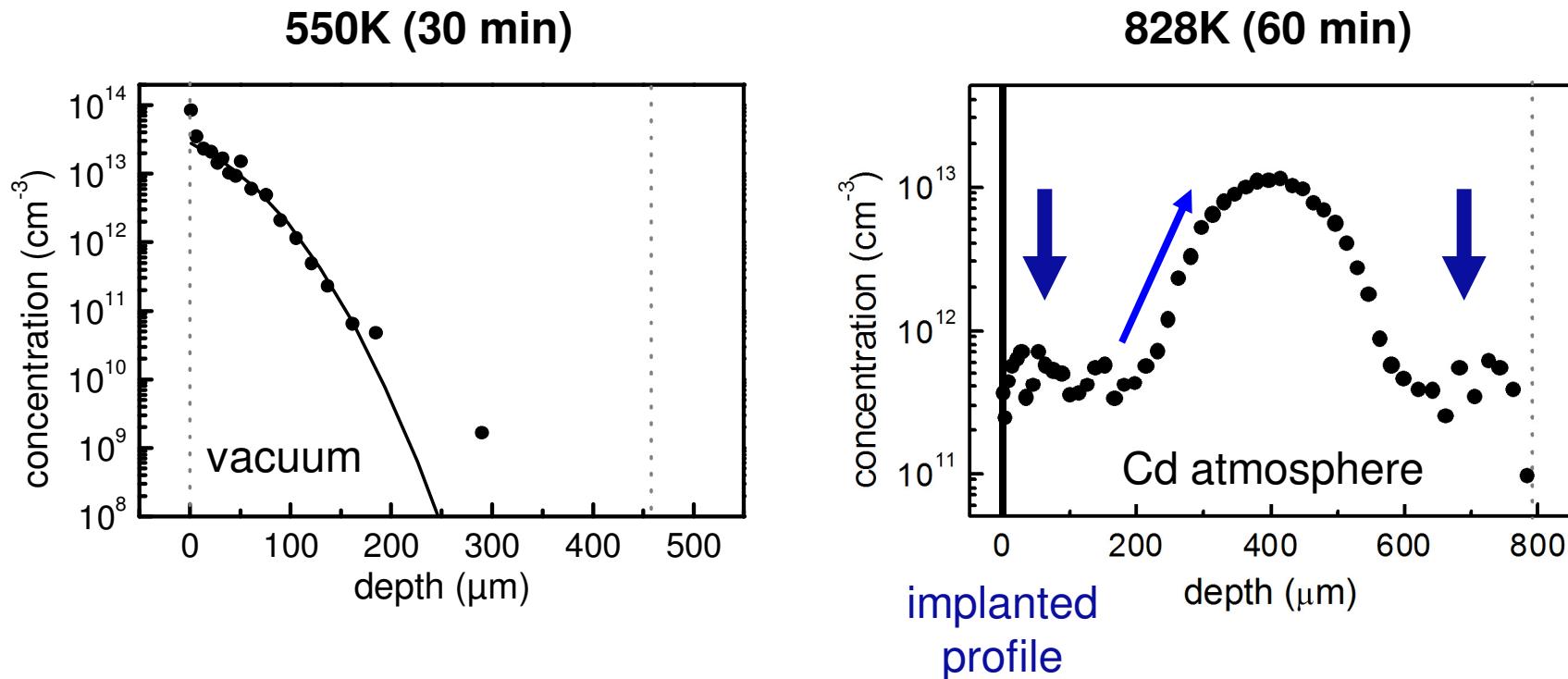


Fig. 2.1. Illustration of Fick's first law

Diffusion of ^{111}Ag in CdTe



- no loss of activity
- diffusion towards increasing Ag concentration

Fick's First Law

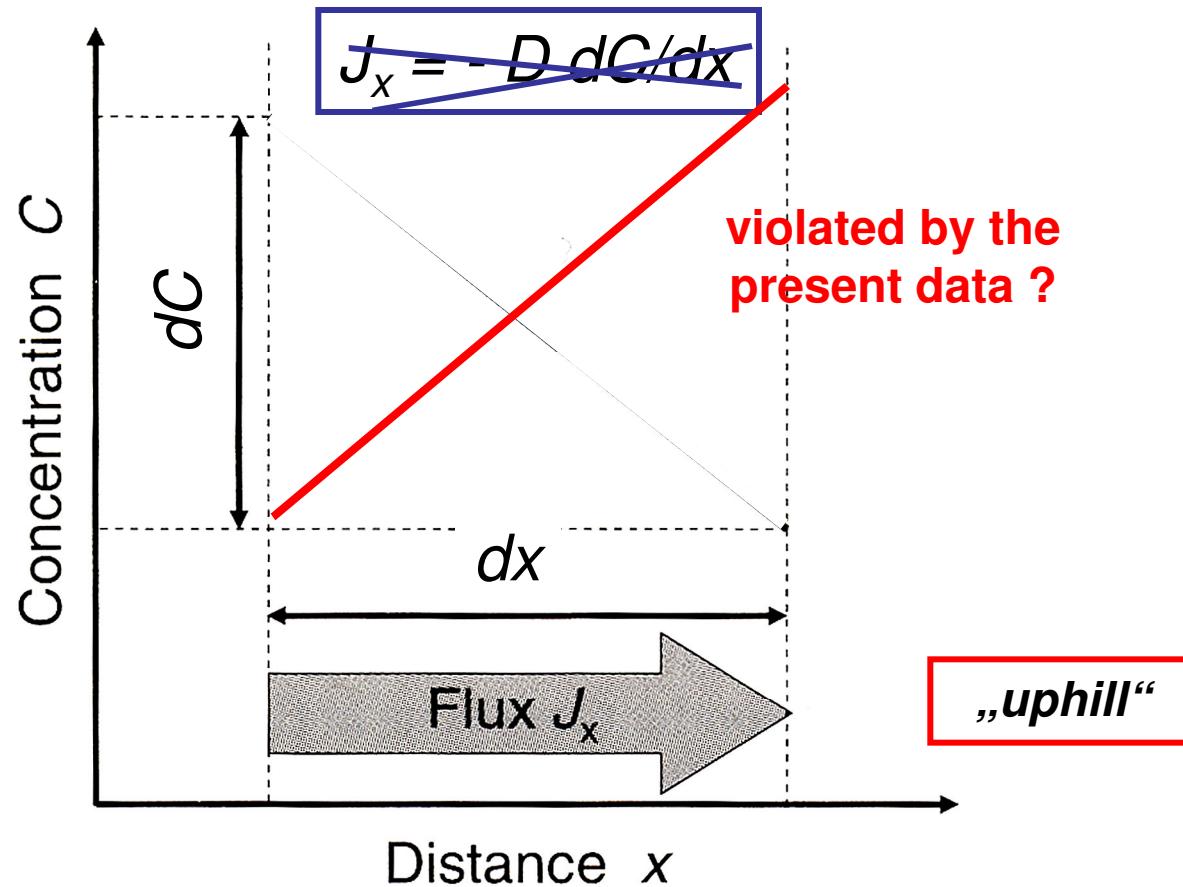


Fig. 2.1. Illustration of Fick's first law

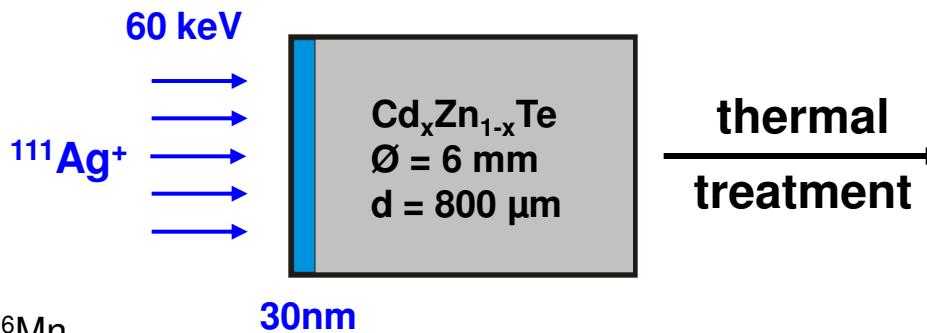
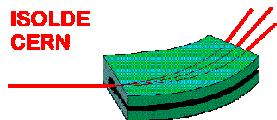
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 - Semiconductors and *uphill diffusion*
 - *Uphill diffusion* and self-interstitials
 - Self-interstitials and metal layers
- **On-line Diffusion Chamber**

Following the set-up by the Stuttgart group ($T_{1/2} > 10$ min):

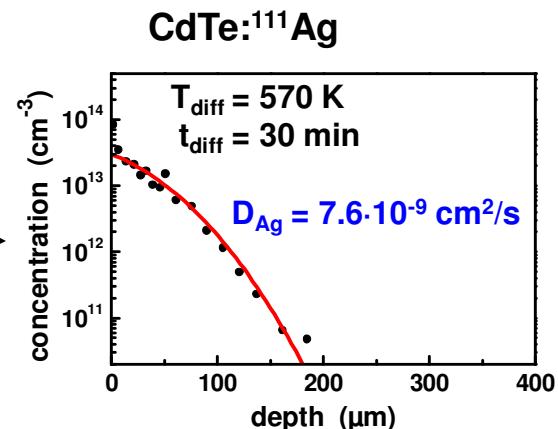
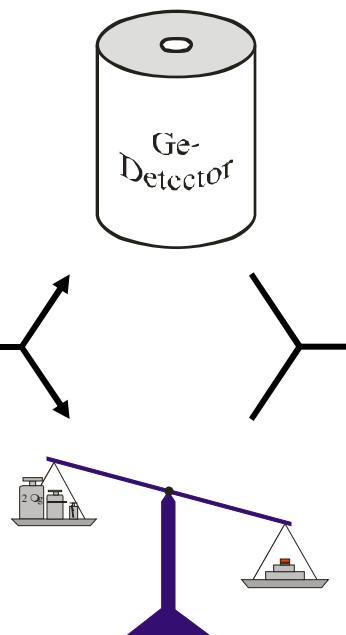
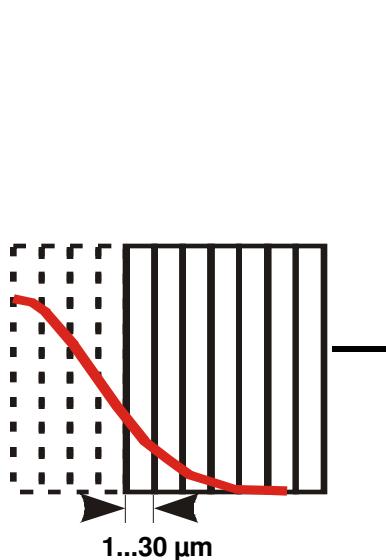
Radiotracer Technique

Implantation



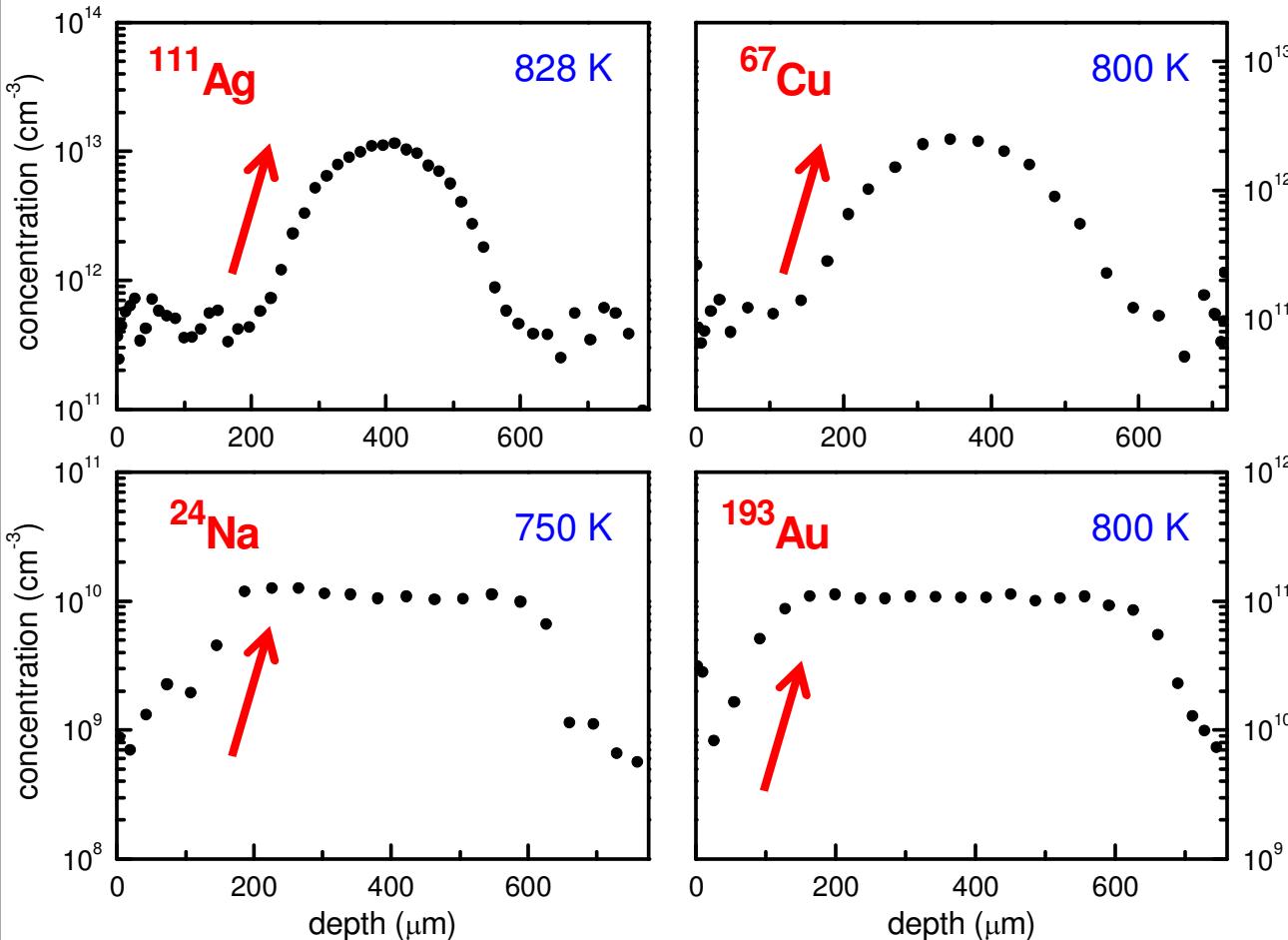
Used isotopes :

^{111}Ag , ^{67}Cu , ^{24}Na , ^{43}K , ^{56}Mn ,
 ^{59}Mn (^{59}Fe), ^{65}Ni , ^{61}Mn (^{61}Co), ^{101}Cd (^{101}Pd), ^{191}Hg (^{191}Pt), ^{193}Hg (^{193}Au)



Experimental Results

Te-saturated CdTe: $t_{\text{diff}} = 60 \text{ min}$, external Cd pressure



CdTe

$t = 0$:
 δ -layer at $x = 0$

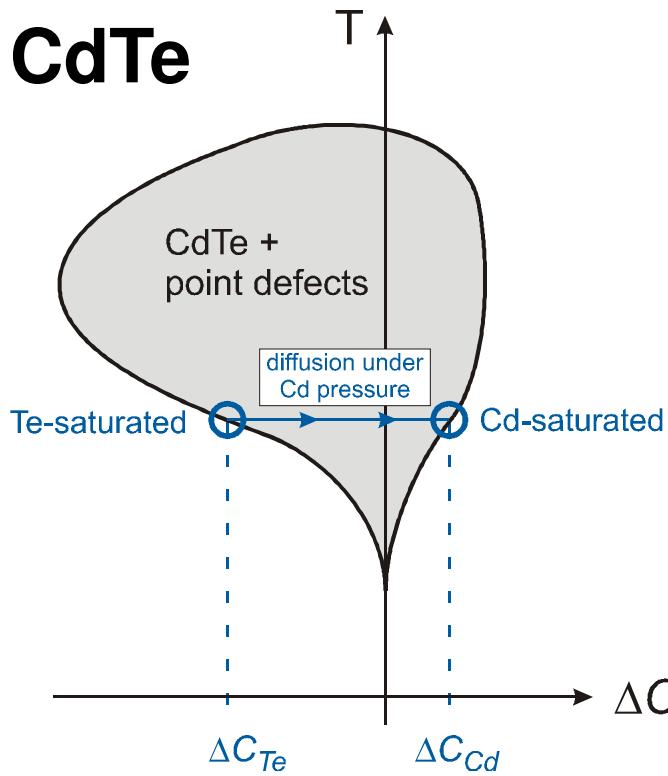
Uphill-diffusion

profile symmetry:
dopant in equilibrium
with host crystal

profile shape:
result of
intrinsic defects

Control of Intrinsic Defects

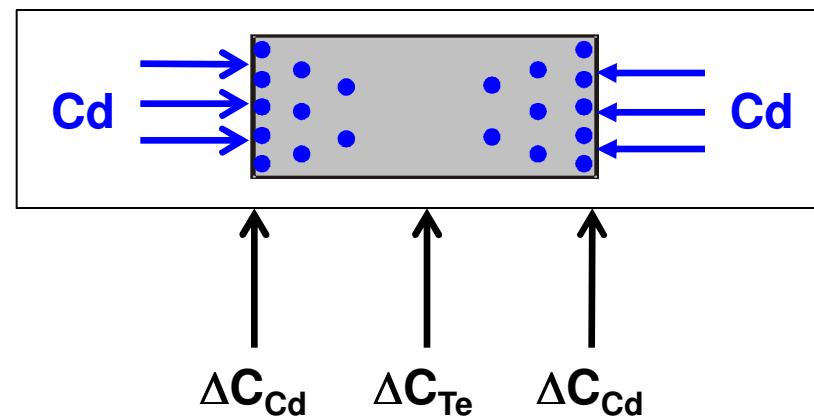
T- ΔC phase diagram (sketch)



Initial CdTe:

$$\Delta C = \Delta C_{Te}$$

external Cd pressure



ΔC : deviation from stoichiometry

Defects Involved

Cd
sublattice

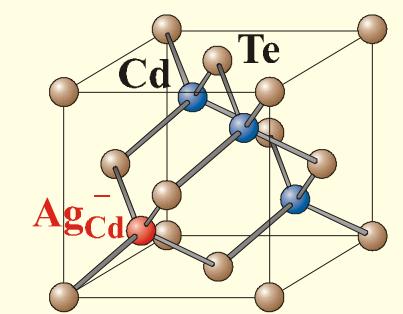
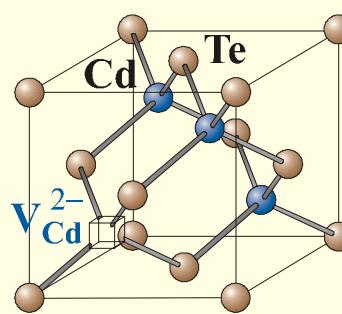
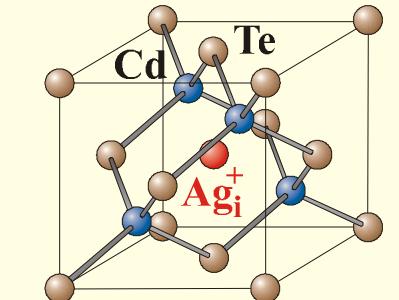
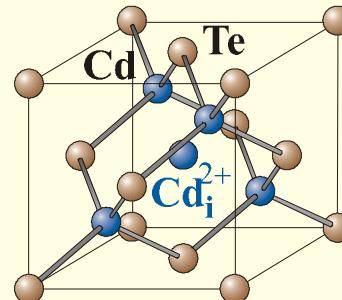
intrinsic

extrinsic

donors

... and all defects
can be charged

acceptors



$$[\Delta C] = [C_{di}] - [V_{cd}] - [A_{cd}]$$

Te sublattice: „perfect“

=> Deviation from stoichiometry

Fick's First Law revised

Particle Flux J

usually

$$J_x = -D \frac{\partial}{\partial x} C$$

C : concentration
(1 species)

in general

$$J_x = -L \frac{\partial}{\partial x} \underline{\mu}$$

$\underline{\mu}$: chemical potentials
(several species)

Fick's First Law revised

Change
in the
concentrations
of

driven by the
chemical potentials

Ag atoms
intrinsic defects
charge carriers

$$d \begin{pmatrix} [\text{Ag}] \\ [\Delta C] \\ [Cq] \end{pmatrix}$$

Modelling of Experimental Results

- interaction of dopants with intrinsic defects
- charge states of extrinsic and intrinsic defects
- profile of ΔC leads to *formation of p/n junctions*
- drift in internal electric field

H. Wolf et al., Physica B 308-310 (2001) 963

H. Wolf et al., Physica B, 340 - 342 (2003) 275 - 279

H. Wolf et al., Phys. Rev. Lett. 94 (2005) 125901.

H. Wolf et al., Defect and Diffusion Forum 237-240 (2005) 491.

F. Wagner et al., Proc. of the 1st Int. Conf. on Diffusion in Solids and Liquids (DSL 2005)

H. Wolf et al., J. Electr. Mater. 35 (2006) 1350.

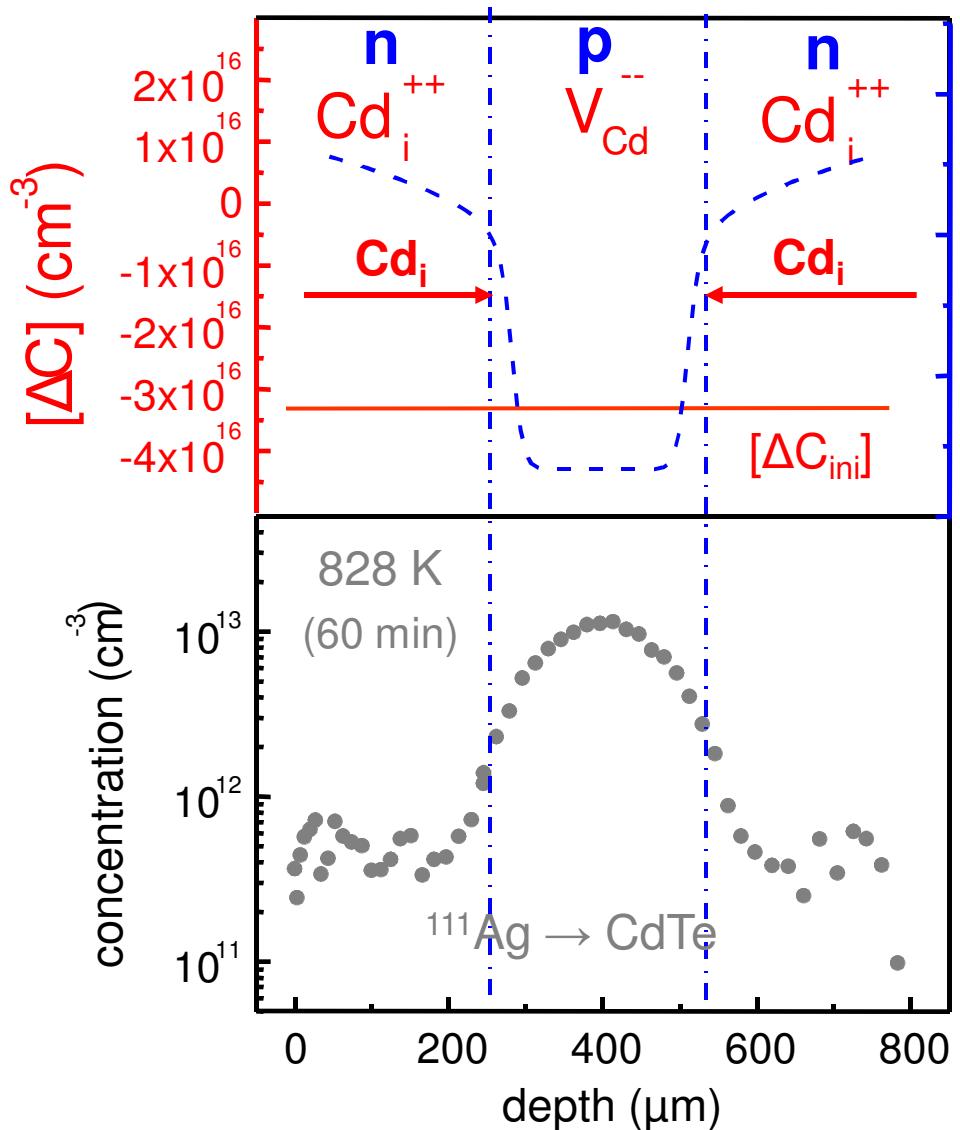
F. Wagner et al., Physica B: Condensed Matter 401-402 (2007) 286-290

H. Wolf et al., Diffusion Fundamentals 8 (2008) 3.1-3.8

F. Wagner, Dissertation, Universität des Saarlandes (2008)

H. Wolf et al., Defect and Diffusion Forum Vols. 289-292 (2009) 587-592

Profile Simulation



$$[\Delta C] = [\text{Cd}_i] - [V_{\text{Cd}}]$$

CdTe is Te-rich $[\Delta C] < 0$

- $[\Delta C]$ determines μ_F

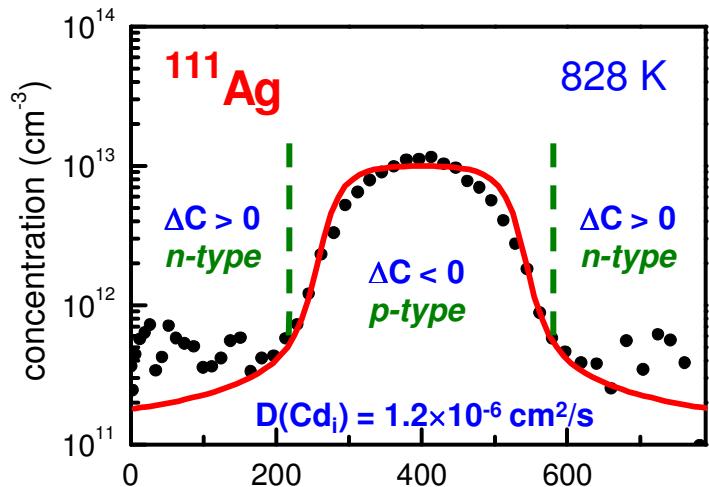
• Cd-atmosphere: Ag - diffusion

- $[\text{Ag}] = [\text{Ag}_i^+]$ highly mobile

- Ag_i^+ behaves like h^+

- Ag profile reflects μ_F and $[\Delta C]$

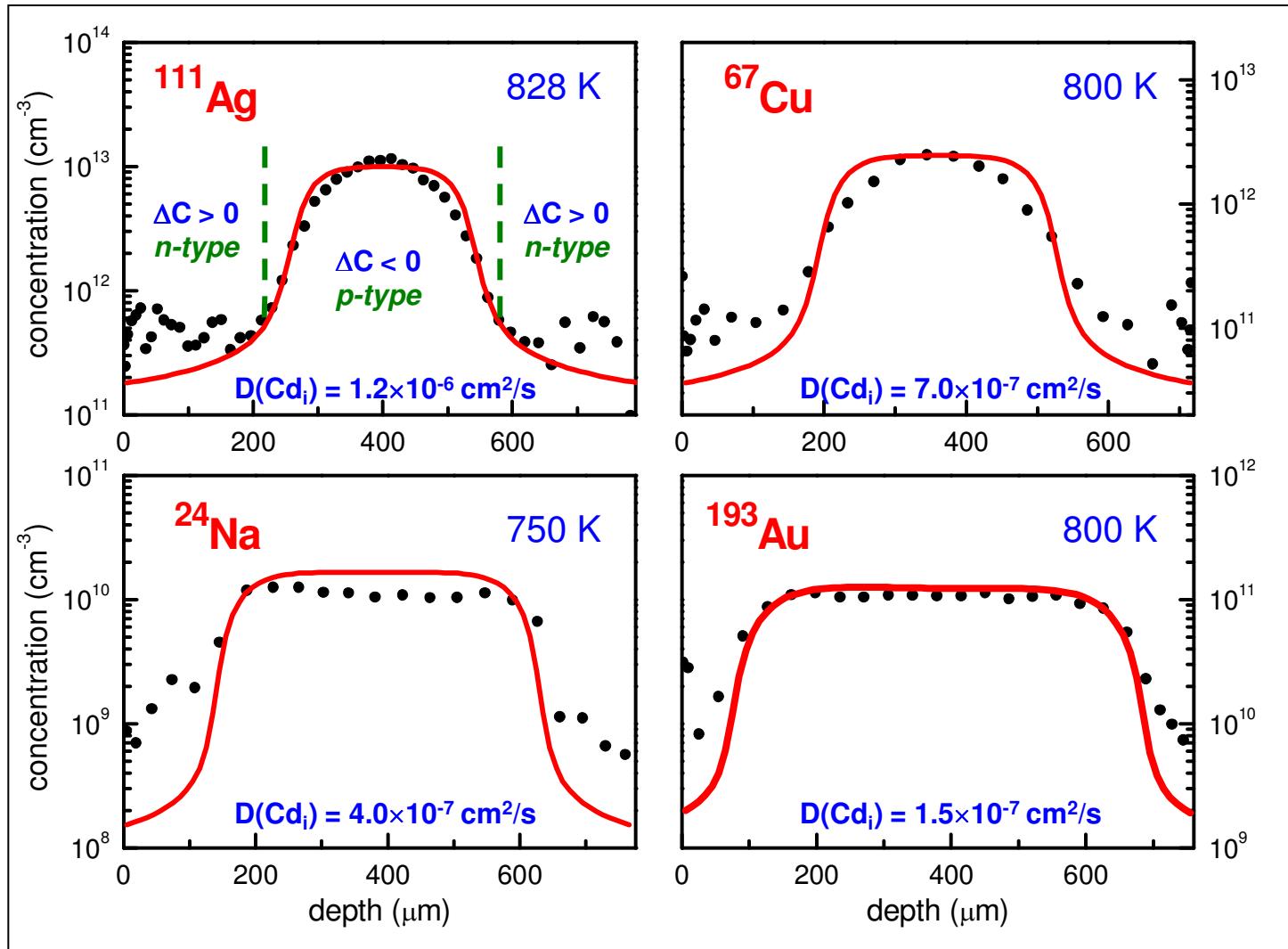
Experiment and Simulation



information about:

- diffusion coefficients
- formation energies
- ionizations energies

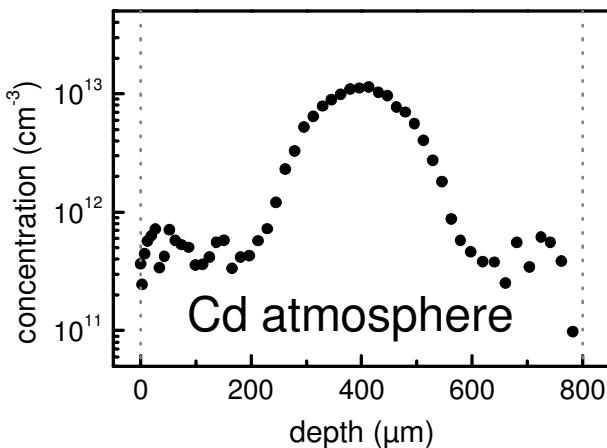
Experiment and Simulation



Ag in Different Semiconductors

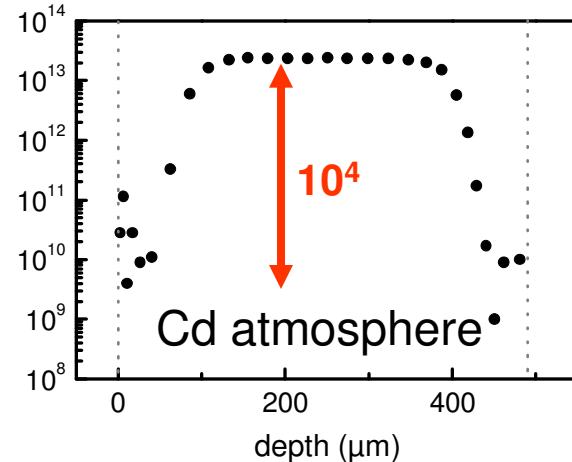
CdTe

828K, 60 min



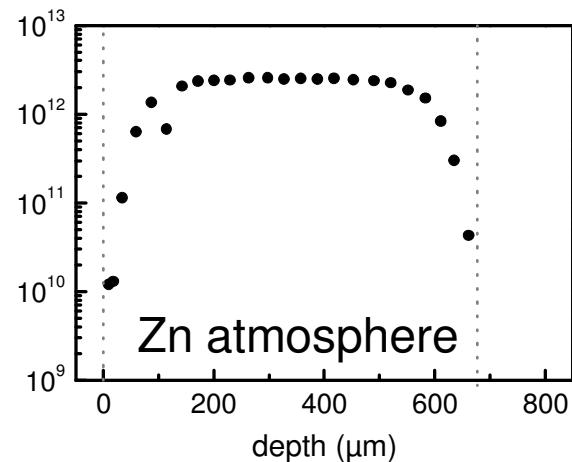
$\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$

828K, 60 min



ZnTe

928K, 24 h



comparable behavior
in different II-VI semiconductors

Uphill Diffusion Profiles in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$

Matrix Isotope

Ia



IIa



VIII

VIII



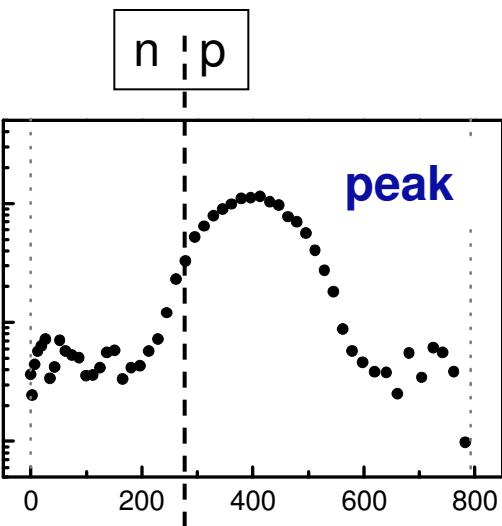
IIIa

IVa

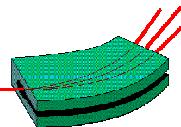
Va

VIa

VIIa



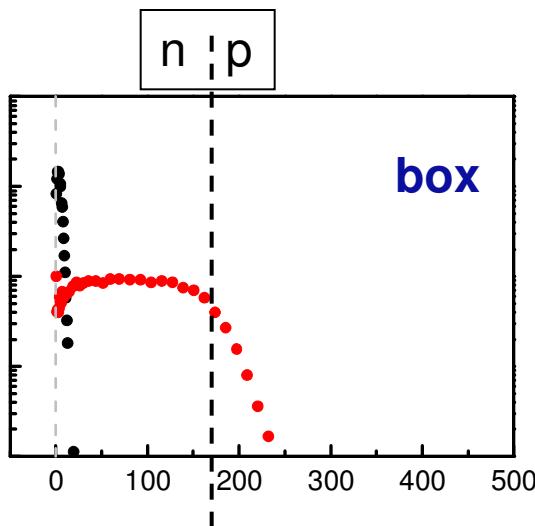
ISOLDE
CERN



Box shaped profiles in Cd_{0.97}Zn_{0.03}Te

Matrix

Isotope



Ia



IIa



IIIb IVb Vb VIb VIIb



VIII



Ib IIb

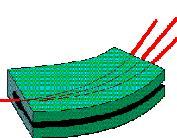


Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr



ISOLDE

CERN



VIII



IIIa



IVa



Va



VIa

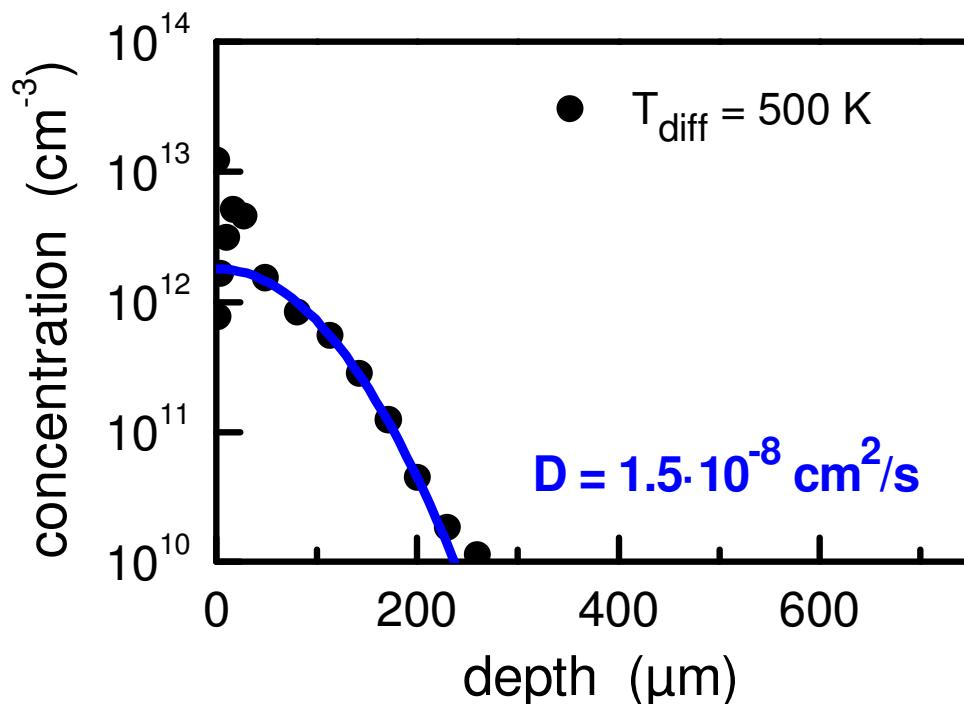


VIIa

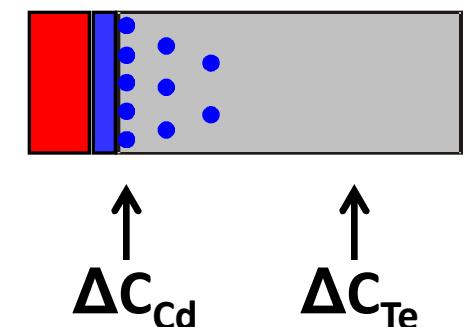


Influence of Metal Layers

^{111}Ag in CdTe



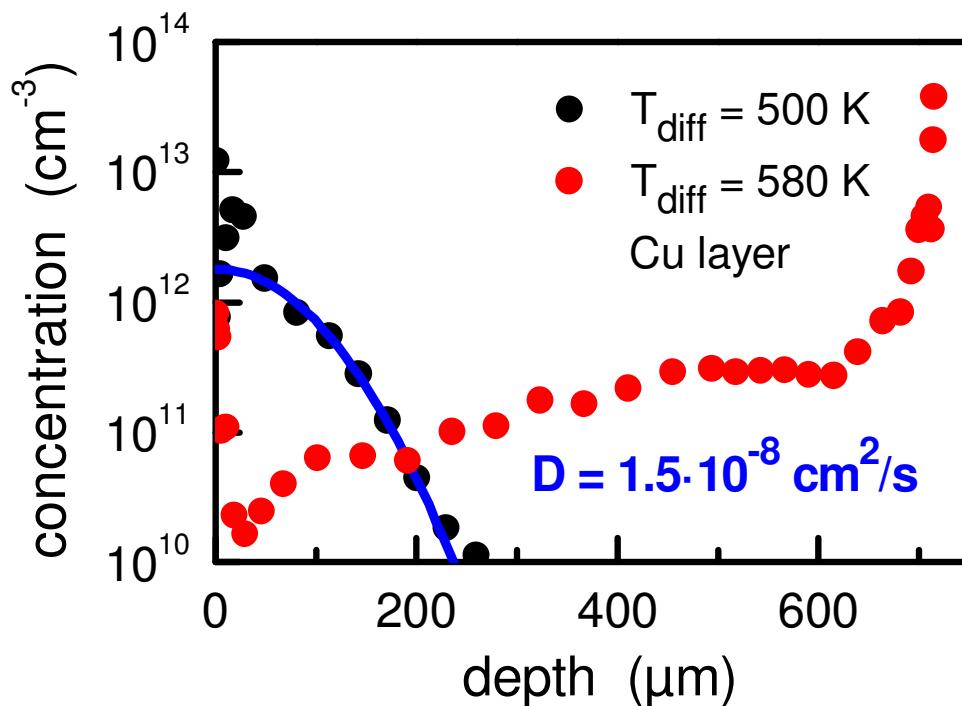
plus copper
metal layer



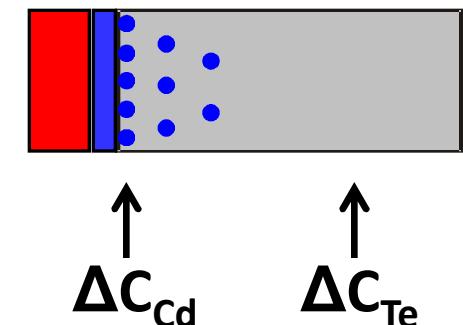
Te-saturated ($\Delta C_{\text{ini}} = \Delta C_{\text{Te}}$)

Influence of Metal Layers

^{111}Ag in CdTe



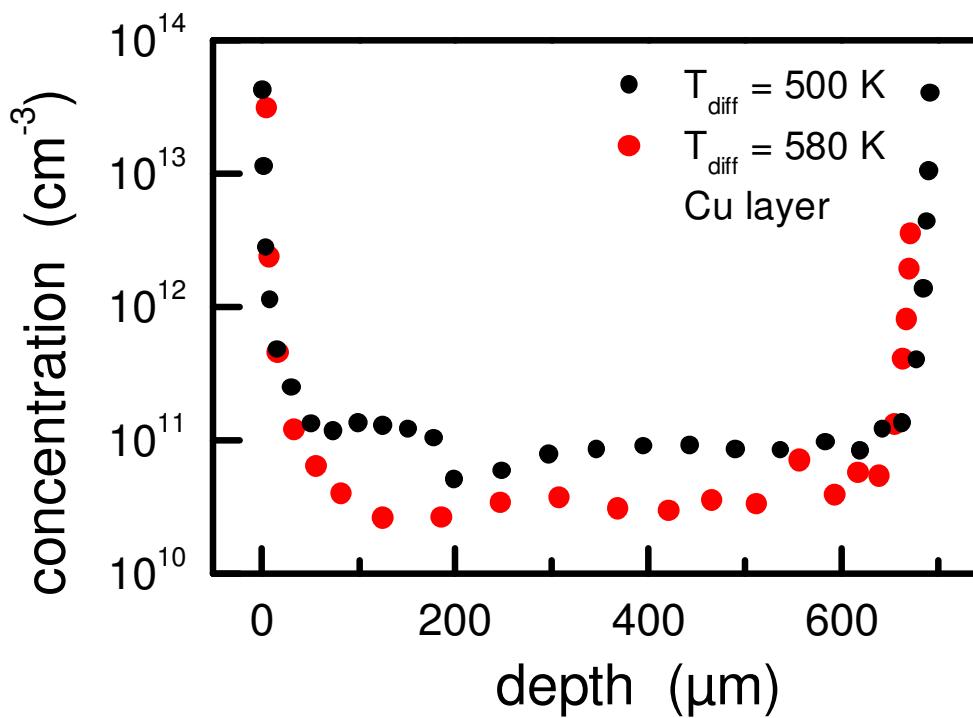
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Te-saturated ($\Delta C_{\text{ini}} = \Delta C_{\text{Te}}$)

Influence of Metal Layers

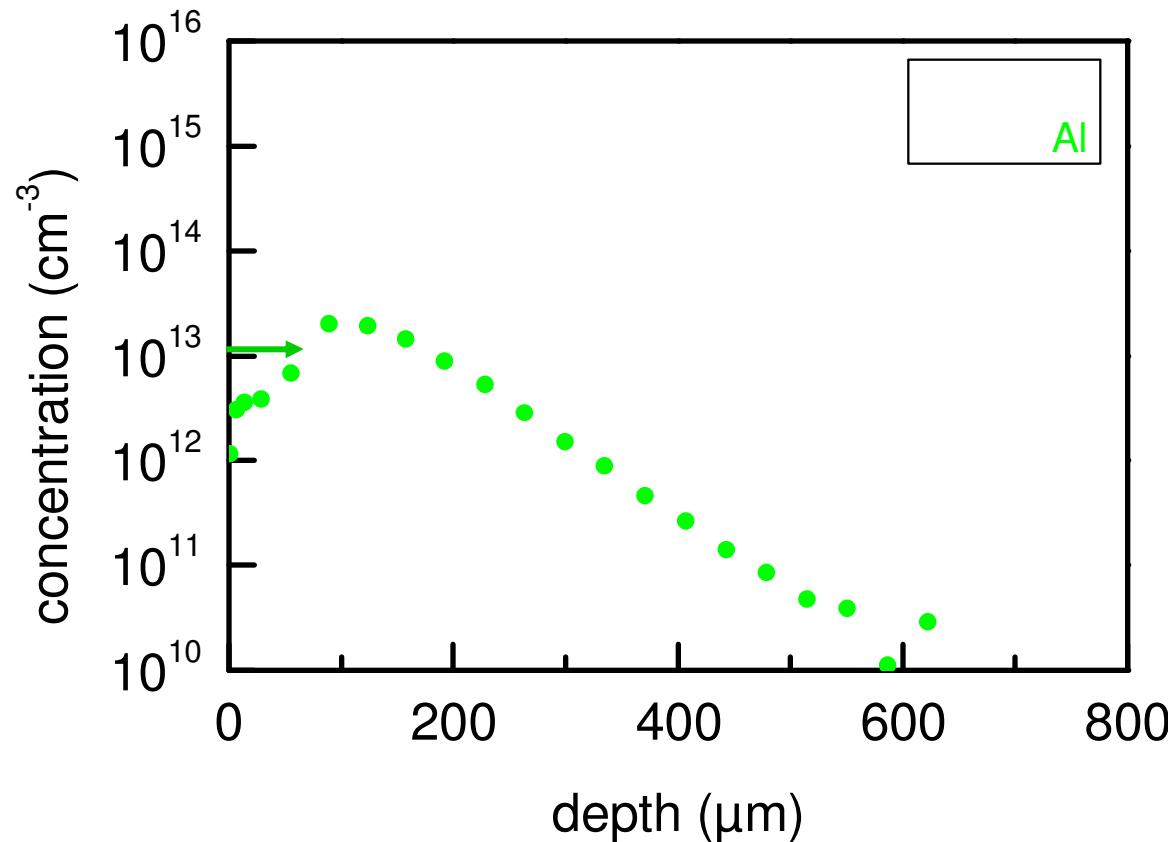
^{111}Ag in CdTe



Cd-saturated ($\Delta C_{\text{ini}} = \Delta C_{\text{Cd}}$)

Influence of Metal Layers

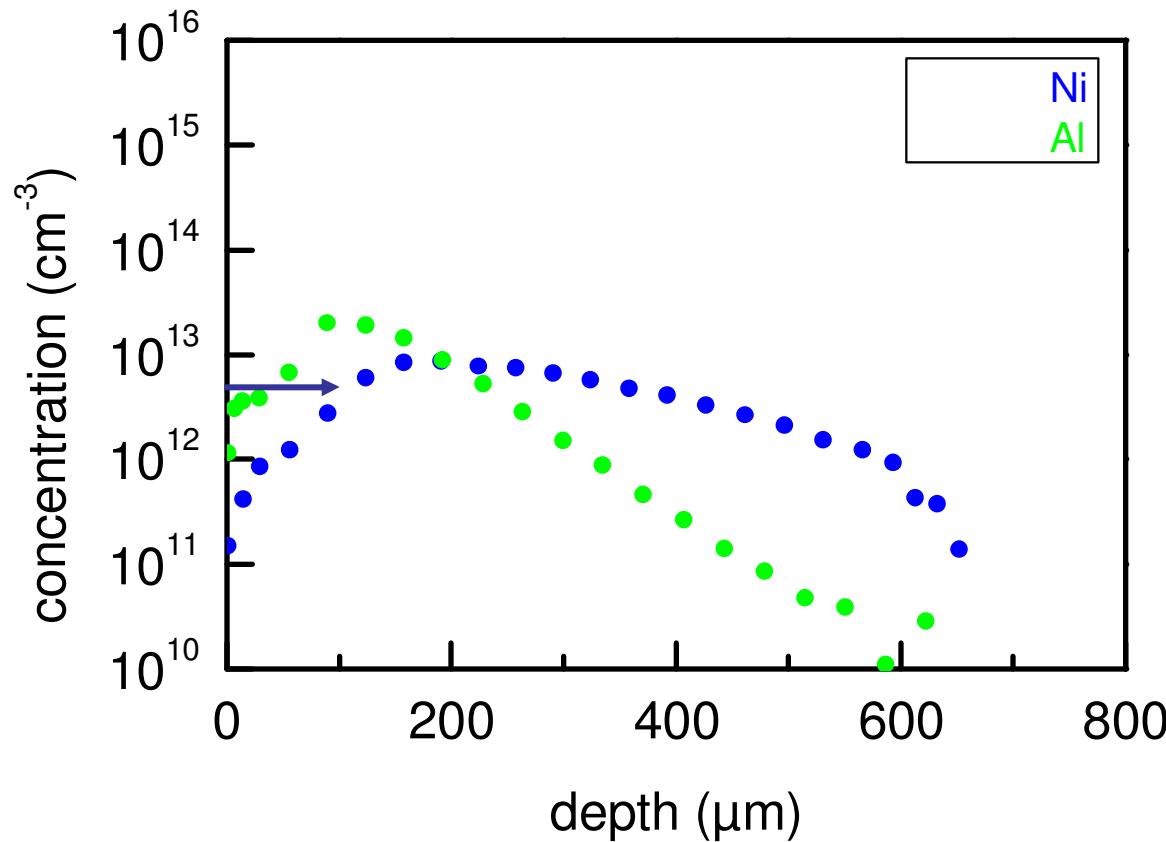
^{111}Ag in CdTe (580 K)



Te-saturated ($\Delta C_{\text{ini}} = \Delta C_{\text{Te}}$)

Influence of Metal Layers

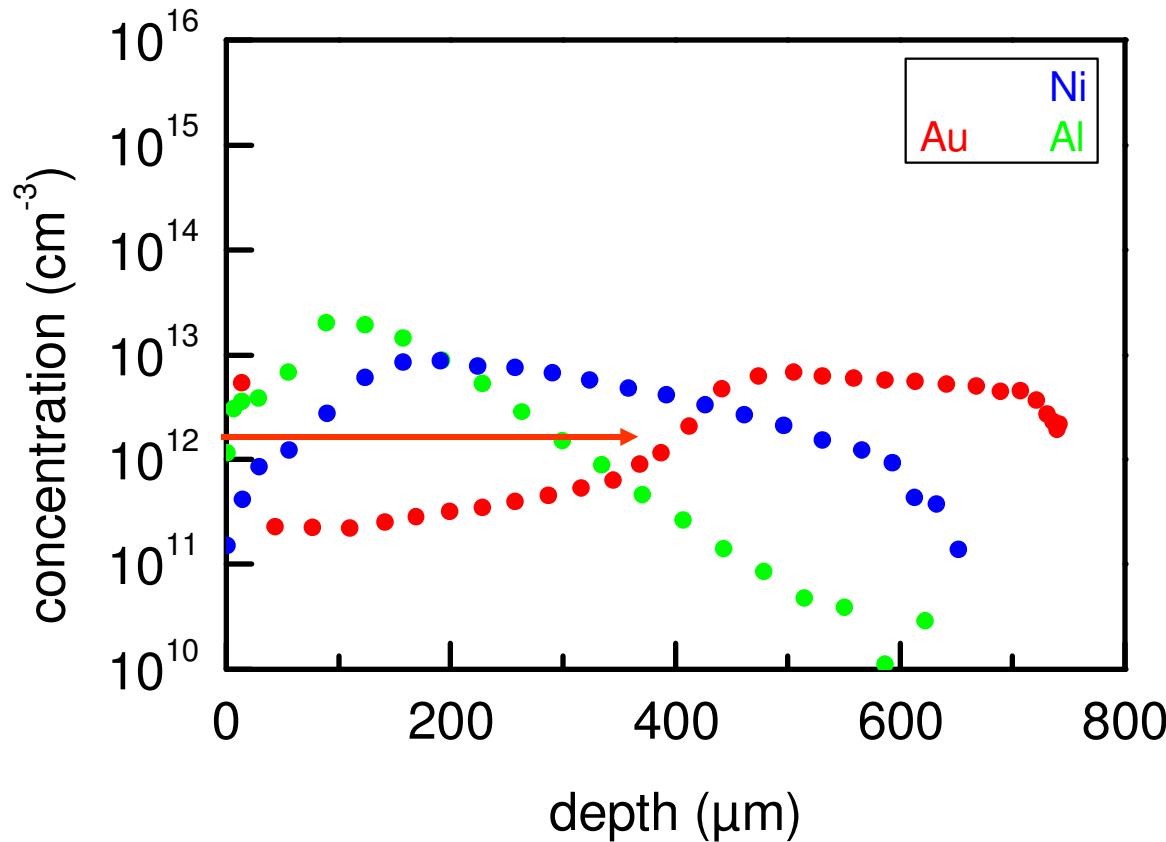
^{111}Ag in CdTe (580 K)



Te-saturated ($\Delta C_{\text{ini}} = \Delta C_{\text{Te}}$)

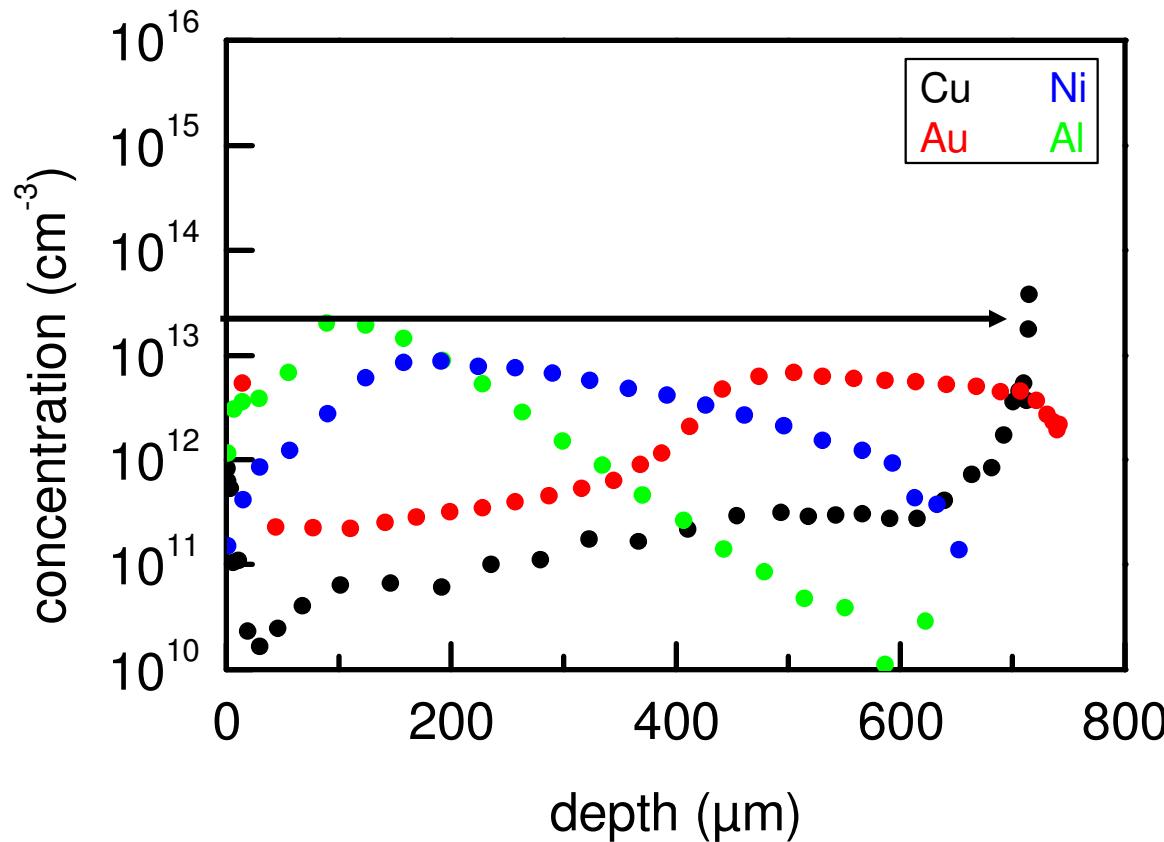
Influence of Metal Layers

^{111}Ag in CdTe (580 K)



Influence of Metal Layers

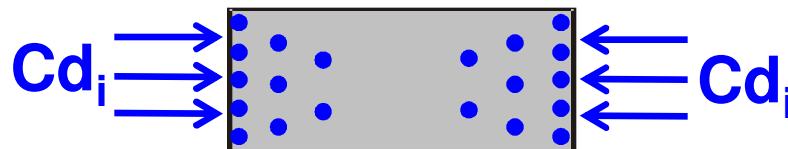
^{111}Ag in CdTe (580 K)



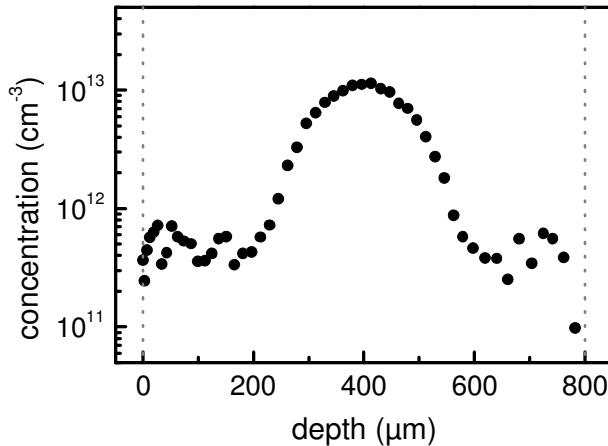
Te-saturated ($\Delta C_{\text{ini}} = \Delta C_{\text{Te}}$)

Uphill Diffusion

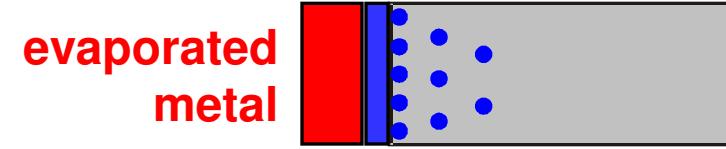
Injection of Cd Interstitials by



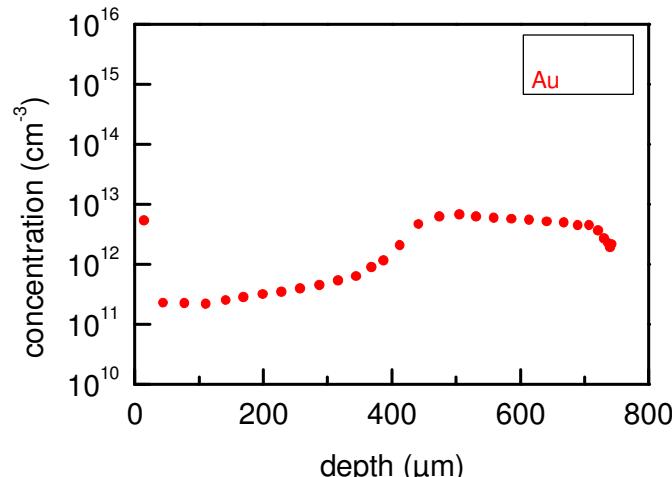
$$\Delta C_{Cd} \quad \Delta C_{Te} \quad \Delta C_{Cd}$$



*external Cd vapour pressure
(symmetric Ag profile)*

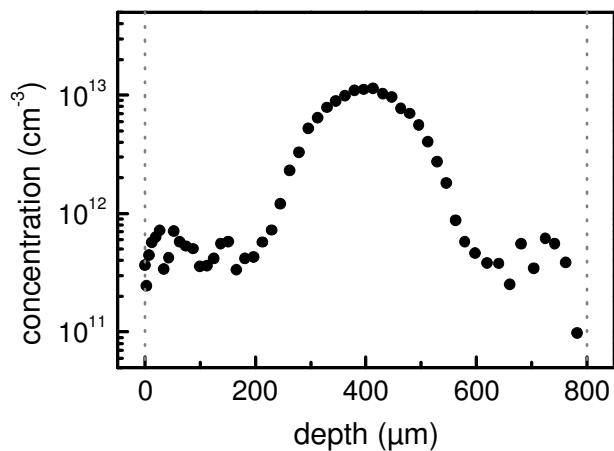
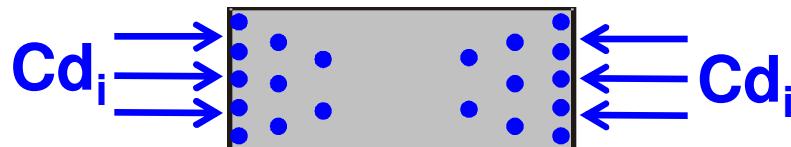


$$\Delta C_{Cd} \quad \Delta C_{Te}$$

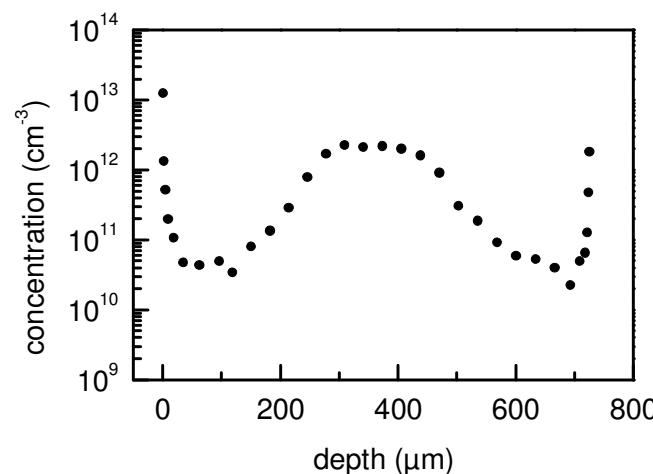
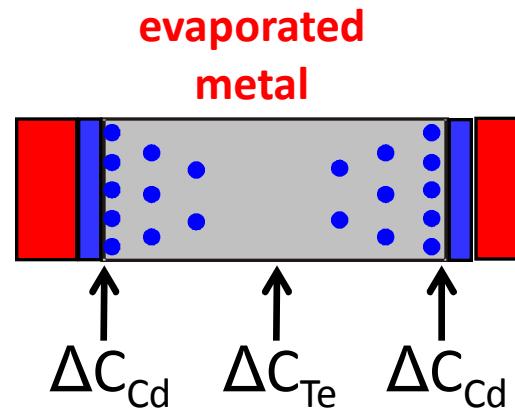


*metal layer evaporated on surface
(asymmetric Ag profile)*

Uphill Diffusion

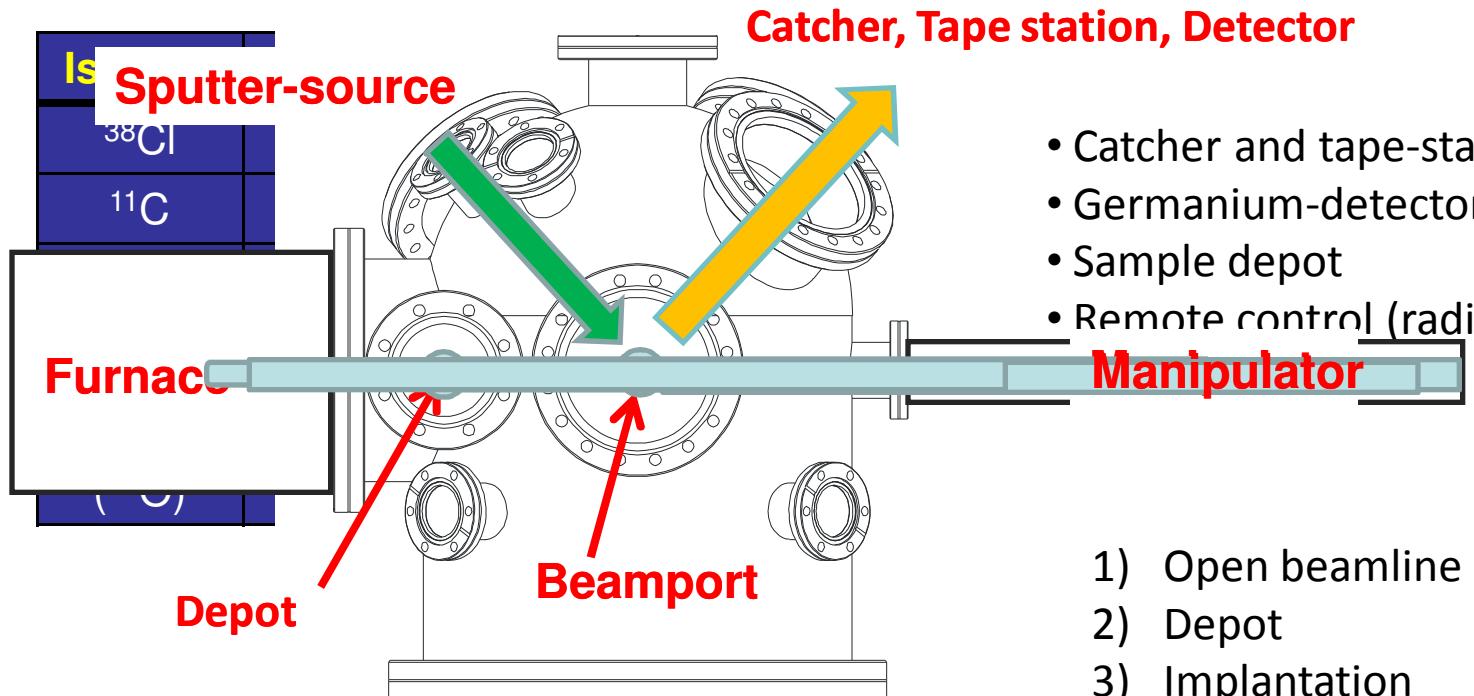


*external Cd vapour pressure
(symmetric Ag profile)*



at 550 K

On-line Diffusion Chamber

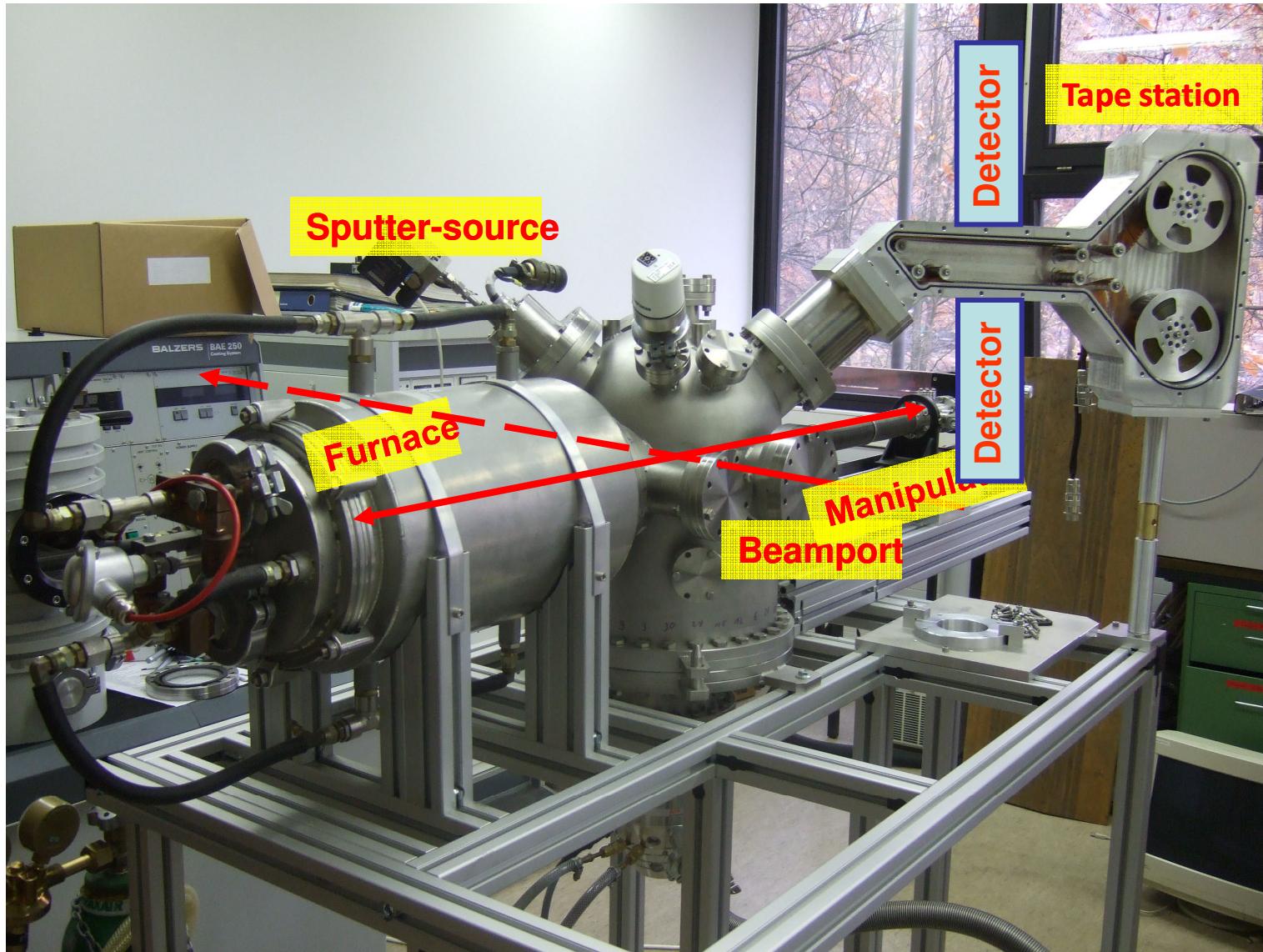


- Catcher and tape-station
- Germanium-detector + "PET"
- Sample depot
- Remote control (radioprotection)

Manipulator

- 1) Open beamline
- 2) Depot
- 3) Implantation
- 4) Annealing
- 5) Sputtering

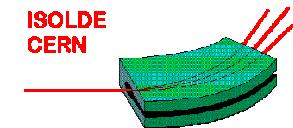
On-line Diffusion Chamber



Summary

1. Diffusion experiments in binary semiconductors

Importance of radioactive isotopes at ISOLDE :
elements, implantation, purity.

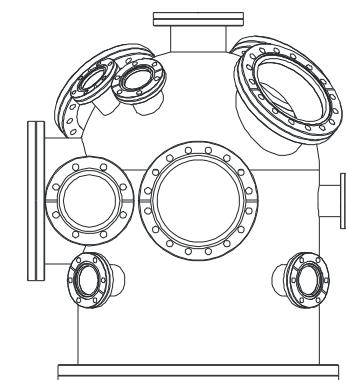
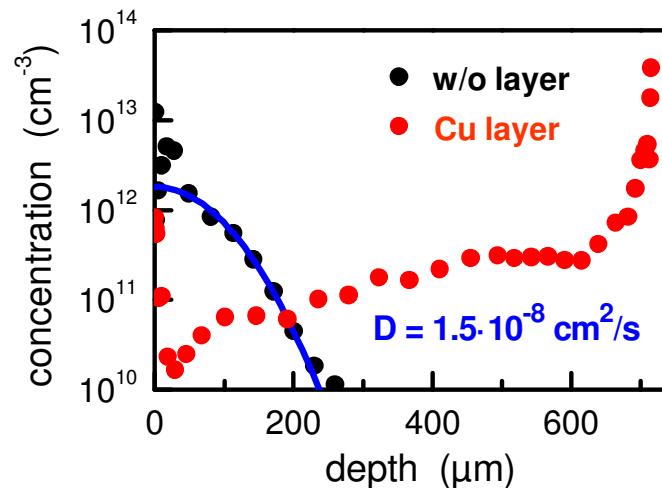
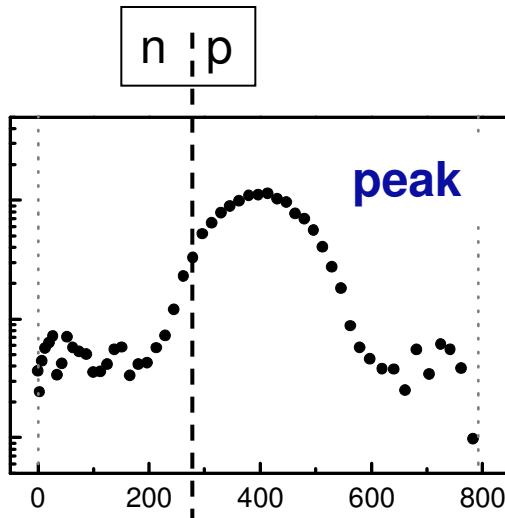


2. Observation and understanding of unusual diffusion profiles

General formulation of Fick's law :
uphill diffusion, quantitativ understanding, metal layers.

3. On-line diffusion chamber for short-lived isotopes

Access to well-needed light elements.



Thanks to ...

Uni Münster:

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R. Vianden
D. Eversheim

CERN:

ISOLDE Collaboration

BMBF for financial support

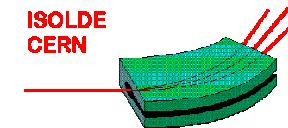


... you for
your attention

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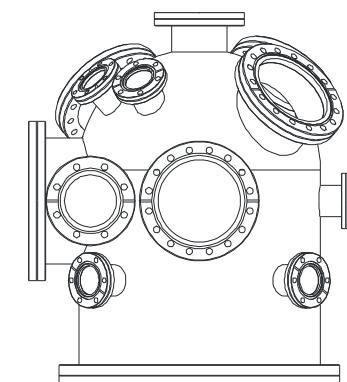
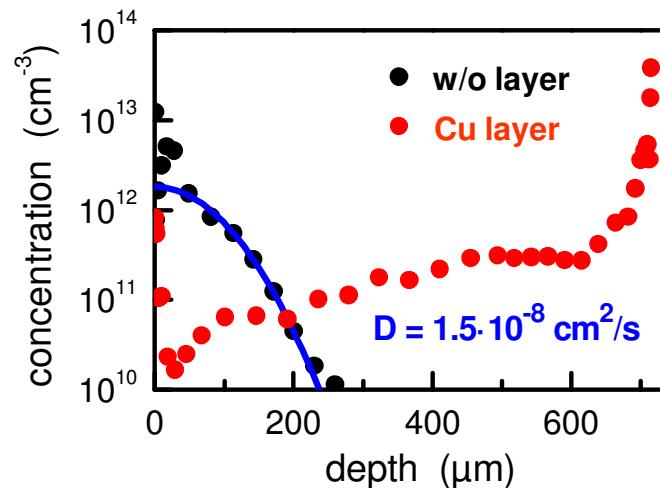
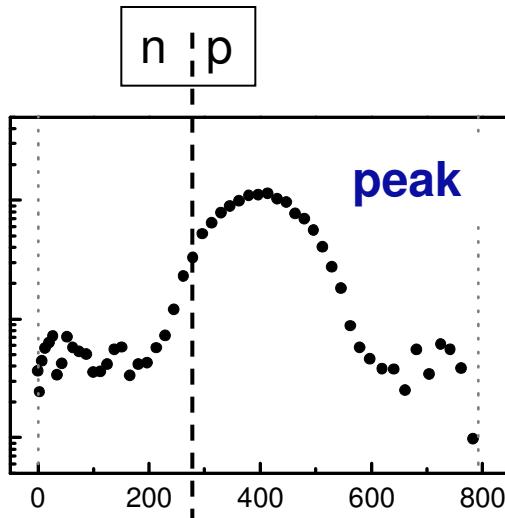


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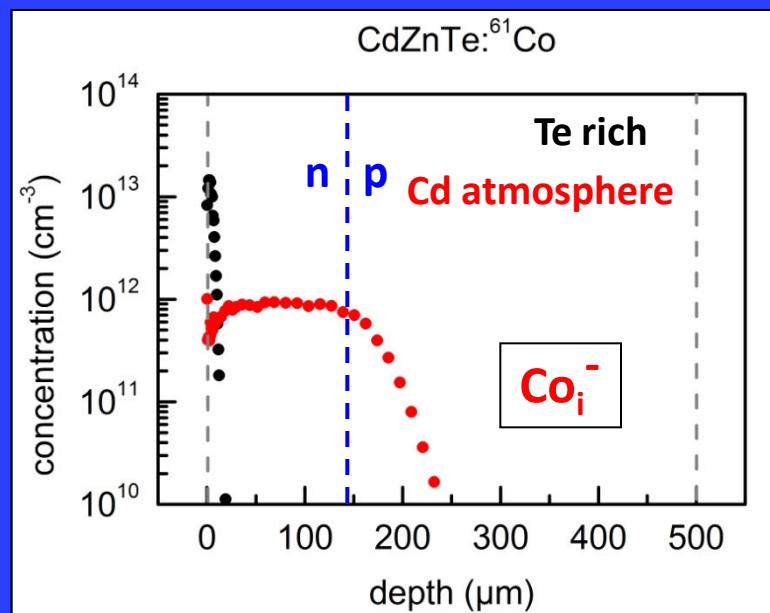
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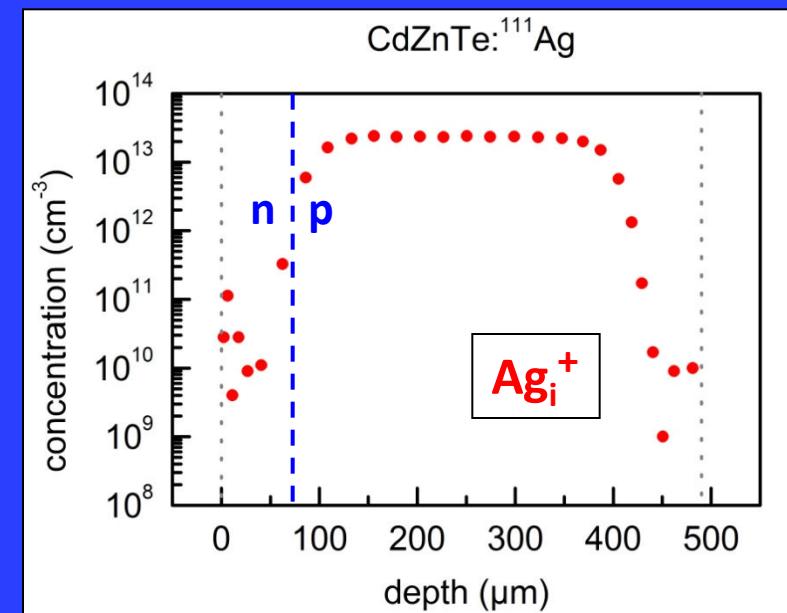
Access to well-needed light elements.



^{61}Co ($t_{1/2} = 1,65 \text{ h}$) diffusion in CdZnTe



$T_{\text{diff}} = 800 \text{ K}$
 $t_{\text{diff}} = 30 \text{ min}$
 $t_{\text{diff}} = 60 \text{ min}$



Te rich (p-type): \rightarrow substitutional incorporation?

Cd rich (n-type): \rightarrow Co incorporated as Co_i

Future : Short Lived Isotopes

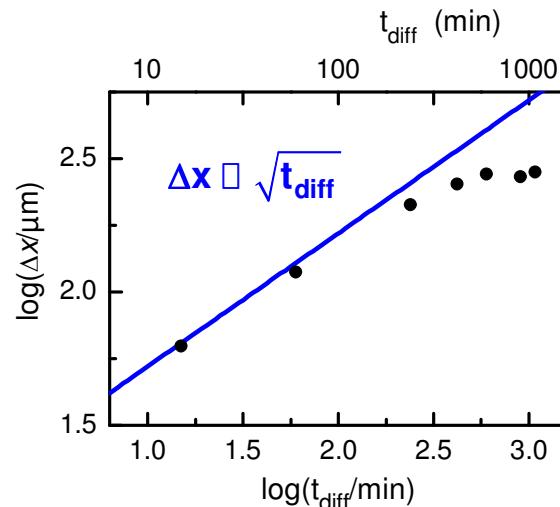
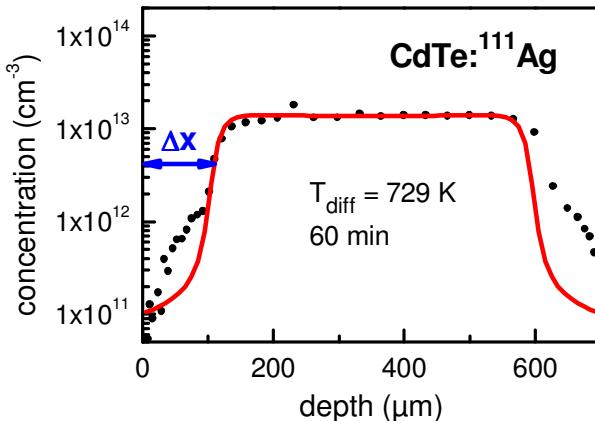
On-line diffusion chamber

Following the set-up by the Stuttgart group ($T_{1/2} > 10$ min):

Isotope	$T_{1/2}$
^{38}Cl	37,3 min
^{11}C	20,38 min
^{13}N	9,96 min
^{29}Al	6,6 min
(^{15}O)	122 s

- Diffusion of C, N and O in semiconductors
- Self-diffusion in Al and in Al alloys
- Diffusion of C, N, and O in grain boundaries of nanomaterials

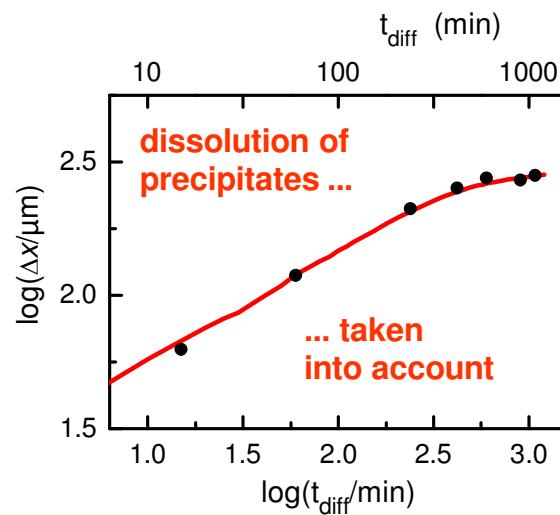
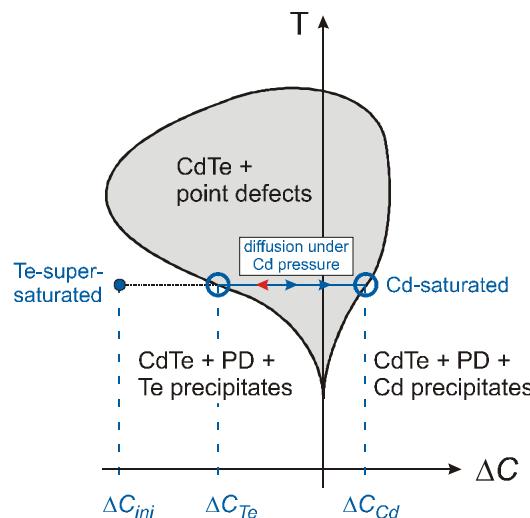
profile analysis



model predicts:

$$\Delta x \propto \sqrt{t_{\text{diff}}}$$

taking into account dissolution of precipitates:
quantitative description of $\Delta x(t_{\text{diff}})$



effective $D(\text{Cd}_i)$ depends on

- density and size
- dissolution rate

of precipitates

used samples:
different with respect to precipitates

defects taken into account

charge states of defects:

$\text{Cd}_i^0, \text{Cd}_i^+, \text{Cd}_i^{2+}$	<i>donor</i>	$\}$	<i>intrinsic (6)</i>
$\text{V}_{\text{Cd}}^0, \text{V}_{\text{Cd}}^-, \text{V}_{\text{Cd}}^{2-}$	<i>acceptor</i>		
$\text{Ag}_i^0, \text{Ag}_i^+$	<i>donor</i>	$\}$	<i>extrinsic (4)</i>
$\text{Ag}_{\text{Cd}}^0, \text{Ag}_{\text{Cd}}^-$	<i>acceptor</i>		
e^-, h^+	<i>free carriers (2)</i>		

defect concentration:

$$[Y] = C_0 \cdot \exp\left(-\frac{F(Y)}{k_B T}\right) \cdot \exp\left(\frac{\mu(Y)}{k_B T}\right)$$

C_0 : number of available lattice sites

Defect interactions
in local equilibrium:

Three chemical
potentials

Three corresponding
concentration quantities

diffusion equations

$$\mu_A := \mu(Ag_i^0)$$

$$[Ag] = [Ag_i] + [Ag_{Cd}]$$

$$\mu_\Delta := \mu(Cd_i^0)$$

$$[\Delta C] = [Cd_i] - [V_{Cd}] - [Ag_{Cd}]$$

$$\mu_q := \mu(e^-)$$

$$[Cq] = (2[V_{Cd}^{2-}] + [V_{Cd}^-] + [Ag_{Cd}^-] + [e^-]) \\ - (2[Cd_i^{2+}] - [Cd_i^+] - [Ag_i^+] - [h^+])$$

unchanged upon
defect reactions

$$\frac{d}{dt}[Ag] = \frac{d}{dx} D_{Ag_i} \cdot [Ag_i] \frac{d}{dx} \mu_A$$

$$\frac{d}{dt}[\Delta C] = \frac{d}{dx} (D_{Cd_i} \cdot [Cd_i] + D_{V_{Cd}} \cdot [V_{Cd}]) \frac{d}{dx} \mu_\Delta$$

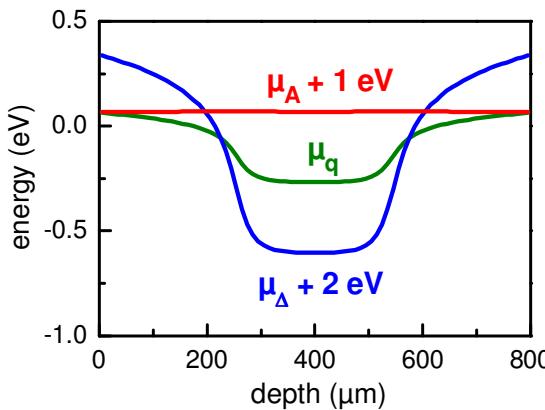
$$\frac{e^2}{\epsilon \cdot \epsilon_0} [Cq] = \frac{d^2}{dx^2} \mu_q$$

$$d \begin{pmatrix} [Ag] \\ [\Delta C] \\ [Cq] \end{pmatrix} = \begin{pmatrix} \frac{\partial [Ag]}{\partial \mu_A} & \frac{\partial [Ag]}{\partial \mu_\Delta} & \frac{\partial [Ag]}{\partial \mu_q} \\ \frac{\partial [\Delta C]}{\partial \mu_A} & \frac{\partial [\Delta C]}{\partial \mu_\Delta} & \frac{\partial [\Delta C]}{\partial \mu_q} \\ \frac{\partial [Cq]}{\partial \mu_A} & \frac{\partial [Cq]}{\partial \mu_\Delta} & \frac{\partial [Cq]}{\partial \mu_q} \end{pmatrix} d \begin{pmatrix} \mu_A \\ \mu_\Delta \\ \mu_q \end{pmatrix}$$

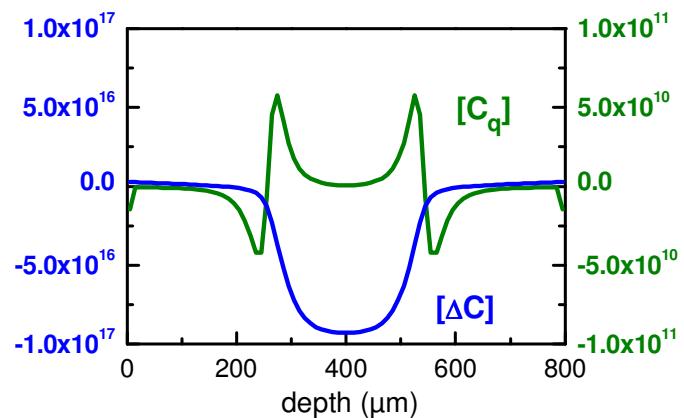
Ag_{Cd} is regarded as *not* mobile

profile analysis

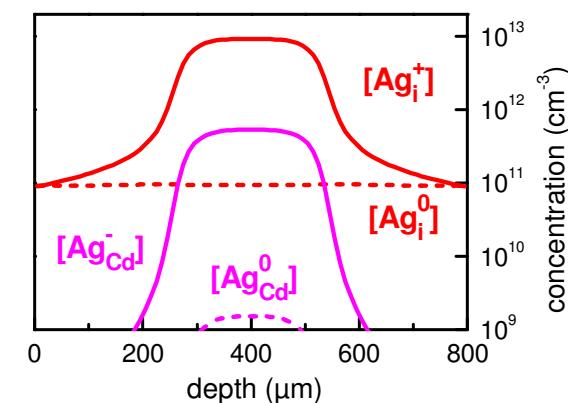
chemical potentials



charge density and stoichiometry deviation



incorporation sites of Ag dopant



Ag dopant in equilibrium with host crystal

pn-transitions formed in front of penetrating Cd_i defects

Ag dopant mostly incorporated as Ag_i^+

essentially the same results for Cu, Au, and Na dopant

$$\mathbf{d} \begin{pmatrix} [\text{Ag}] \\ [\Delta C] \\ [Cq] \end{pmatrix} = \begin{pmatrix} \frac{\partial [\text{Ag}]}{\partial \mu_{\text{Ag}}} & \frac{\partial [\text{Ag}]}{\partial \mu_{\text{Cd}}} & \frac{\partial [\text{Ag}]}{\partial \mu_F} \\ \frac{\partial [\Delta C]}{\partial \mu_{\text{Ag}}} & \frac{\partial [\Delta C]}{\partial \mu_{\text{Cd}}} & \frac{\partial [\Delta C]}{\partial \mu_F} \\ \frac{\partial [Cq]}{\partial \mu_{\text{Ag}}} & \frac{\partial [Cq]}{\partial \mu_{\text{Cd}}} & \frac{\partial [Cq]}{\partial \mu_F} \end{pmatrix} \square \mathbf{d} \begin{pmatrix} \mu_{\text{Ag}} \\ \mu_{\text{Cd}} \\ \mu_F \end{pmatrix}$$

$$D_{\Delta} \approx (D_{Cd_i} \cdot [Cd_i] + D_{V_{Cd}} \cdot [V_{Cd}]) \frac{\partial [Cq]/\partial \mu_F}{(\partial [\Delta C]/\partial \mu_{Cd})(\partial [Cq]/\partial \mu_F) - (\partial [\Delta C]/\partial \mu_F)(\partial [Cq]/\partial \mu_{Cd})}$$

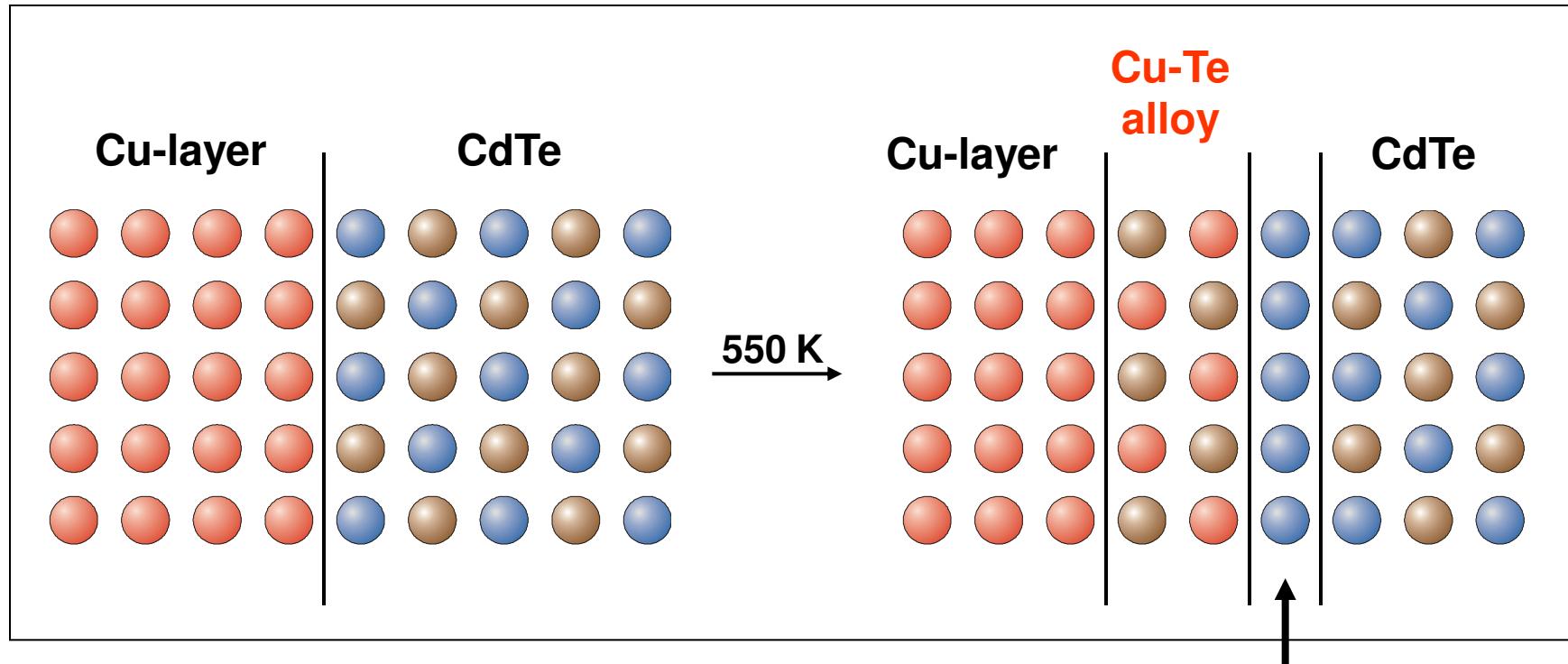
$$\partial [\Delta C]/\partial \mu_{Cd} = [Cd_i] + [V_{Cd}]$$

$$\partial [\Delta C]/\partial \mu_F = \partial [Cq]/\partial \mu_{Cd} = - (2[Cd_i^{2+}] + [Cd_i^+] + 2[V_{Cd}^{2-}] + [V_{Cd}^-])$$

$$\partial [Cq]/\partial \mu_F = (4[Cd_i^{2+}] + [Cd_i^+] + [h^+]) + (4[V_{Cd}^{2-}] + [V_{Cd}^-] + [e^-])$$

$$[Cq] = (2[V_{Cd}^{2-}] + [V_{Cd}^-] + [e^-]) - (2[Cd_i^{2+}] + [Cd_i^+] + [h^+]) = 0$$

Cu and Au layer on surface



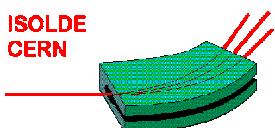
Cd-layer acting as
strong source for
intrinsic defects (Cd_i)

2-3 ML Cd at the interface would be sufficient !

Radioactive Tracers

600 isotopes, 68 elements

Ia	VIII																	
H	He																	
Li	Be																	
3	4																	
Na	Mg	IIIb	IVb	Vb	VIb	VIIb	VIII	Ib	IIb	Al	Si	P	S	Cl	Ar			
11	12	21	22	23	24	25	26	27	28	13	14	15	16	17	18			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi				
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83				



$t_{1/2} > 2 \text{ d}$

$1 \text{ h} < t_{1/2} < 2 \text{ d}$
current

Plasma ion source
Surface ionization (+/-)
 $t_{1/2} <$ Laser ionization
future/current