Observation of vacancies during Zn and Cu diffusion in GaP & GaAs

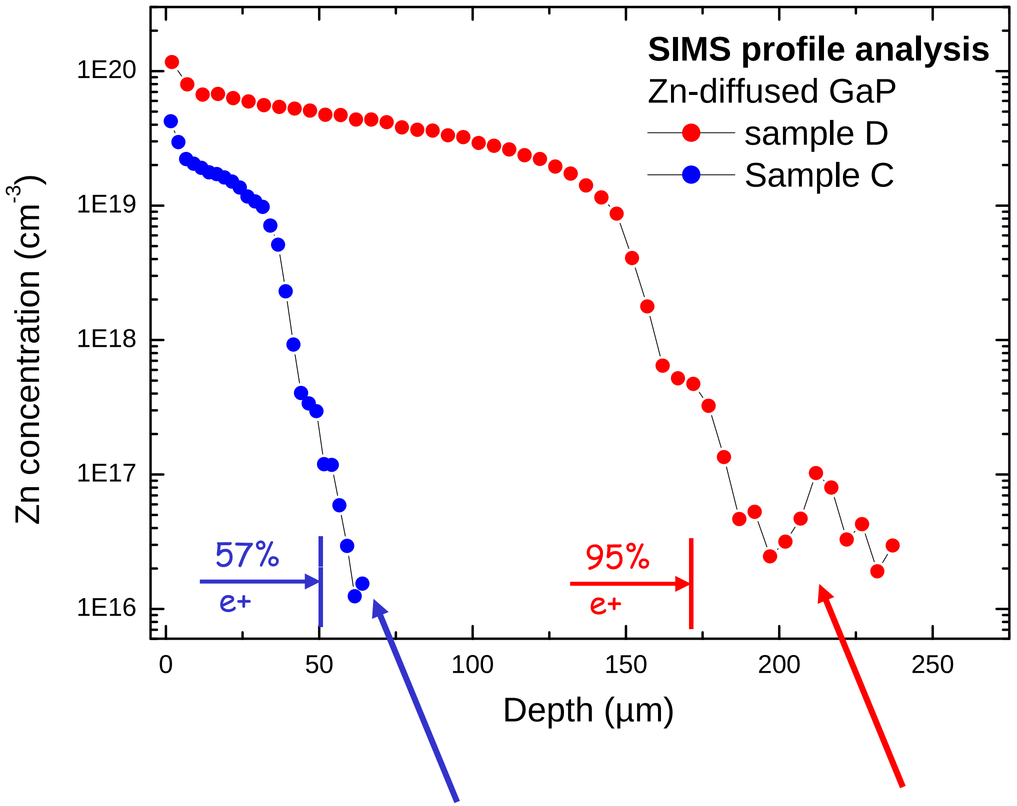
Sample conditions

Experiment	sample	treatment	remarks
Reference	A	as-grown GaP reference sample	negligible low dislocation density, no extended defects
	B	Reference annealing: 95.1 h at 907°C	defined P vapor pressure, but no Zn in ampoule
Diffusion experiments	C	Zn diffusion annealing: 95.1 h at 907°C	defined P vapor pressure, Zn vapor pressure obtained by adding GaP:Zn to the ampoule
	D	Zn Diffusion annealing: 95.1 h at 907°C	defined P vapor pressure, Zn was added as an elementary powder to the ampoule

- Samples were quenched to RT water during diffusion
- Main difference of diffusion experiments: Zn vapor pressure varies due to different Zn source
- Diffusion profiles are distinctly different

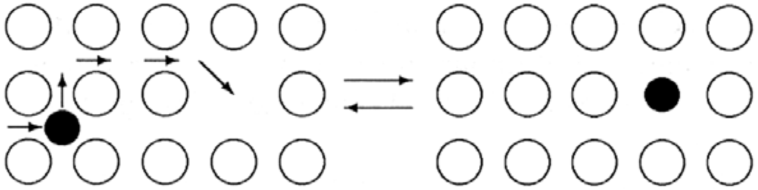
Zn diffusion profiles by SIMS

- Zn diffusion profiles obtained by SIMS at beveled samples (wedge angle 6°)



- expected diffusion model: interstitial-substitutional mechanism (Frank-Turnbull mechanism)
- I_{Ga} and V_{Ga} shall be involved

  (J. Poepping et.al, ICDS-21)
- $Zn_I + V_{Ga} \leftrightarrow Zn_{Ga}$

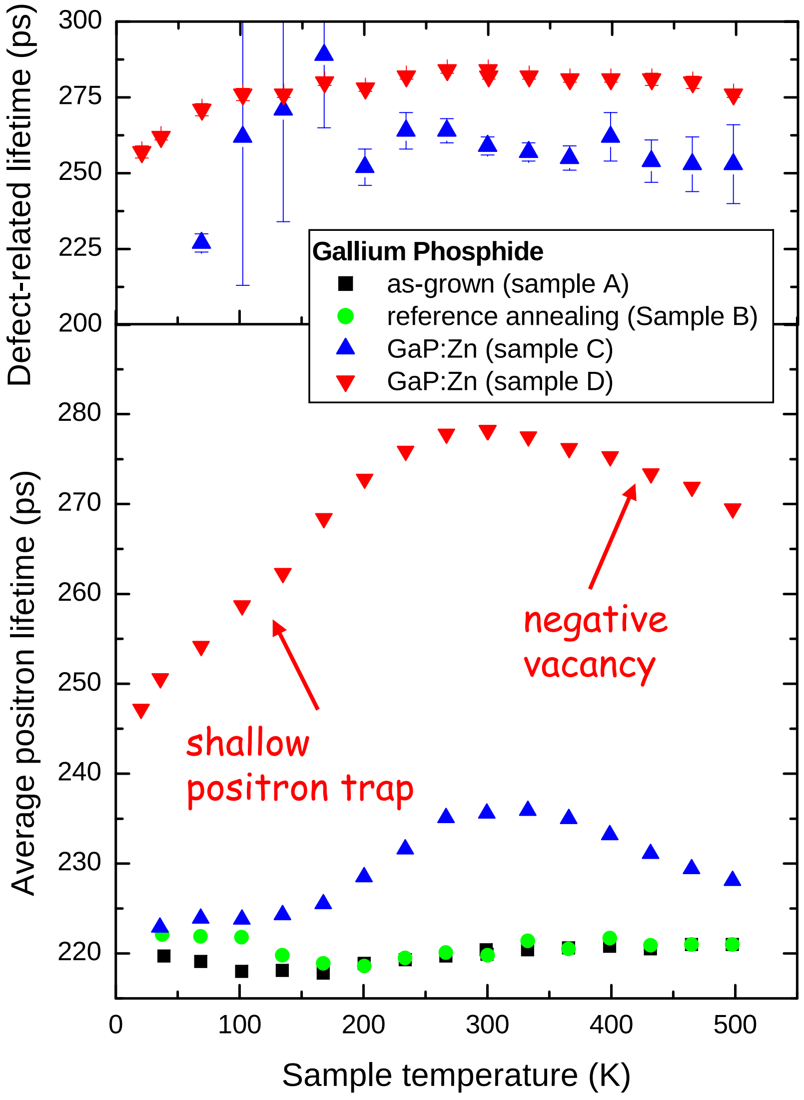


Interstitial-substitutional exchange mechanisms of foreign atom diffusion

Zn source: GaP:Zn sample Zn powder

Diffusion annealing: 95h at 907°C in quartz ampoule

Positron lifetime results



shallow positron trap

negative vacancy

- both reference samples: no trapping
- defect-related lifetime: τ_v = 282 ps
- distinct vacancy signal only after Zn

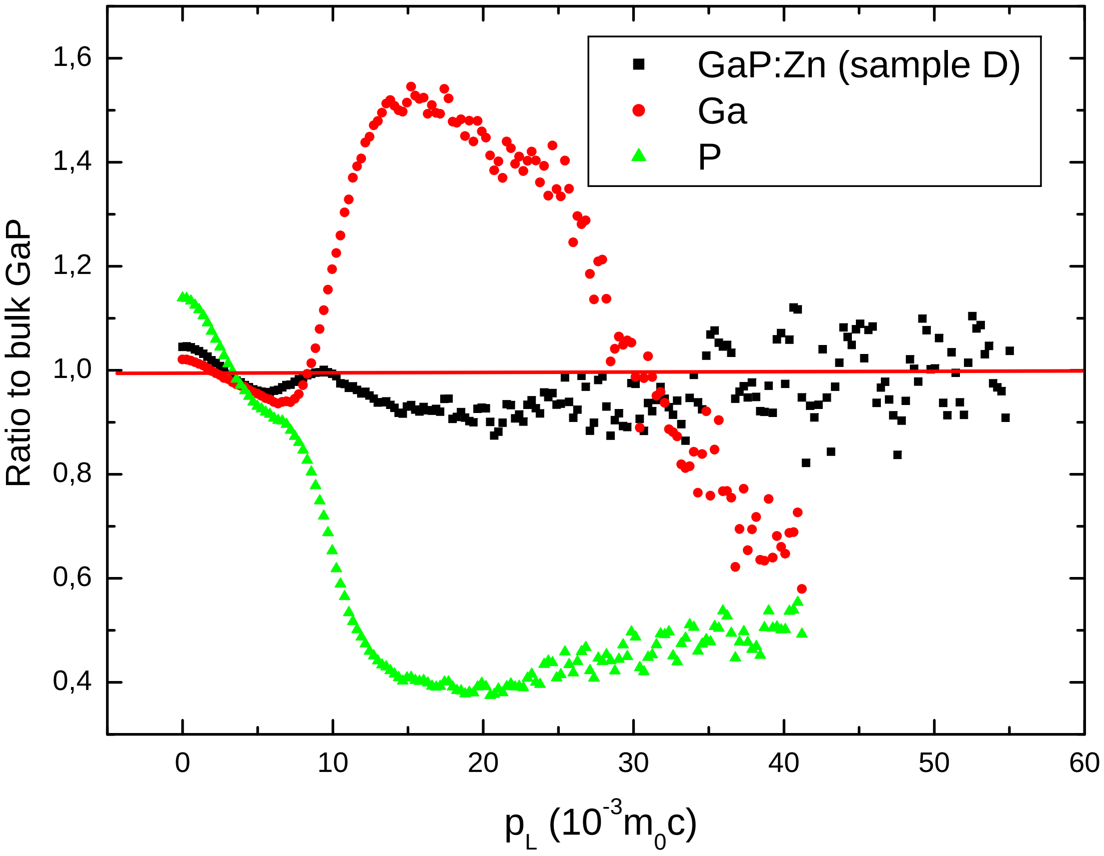
Defect	e^+ lifetime in ps	remarks
GaP bulk	220	
V_{Ga}	258	unrelaxed
	270	3.8% outward relaxation
V_P	244	unrelaxed
	271	6.1% outward relaxation
V_P-Zn_{Ga}	274	6.1% outward relaxation
V_P-V_{Ga}	307	unrelaxed

taking into account the relaxation

- from lifetime: no decision between V_{Ga} and V_P

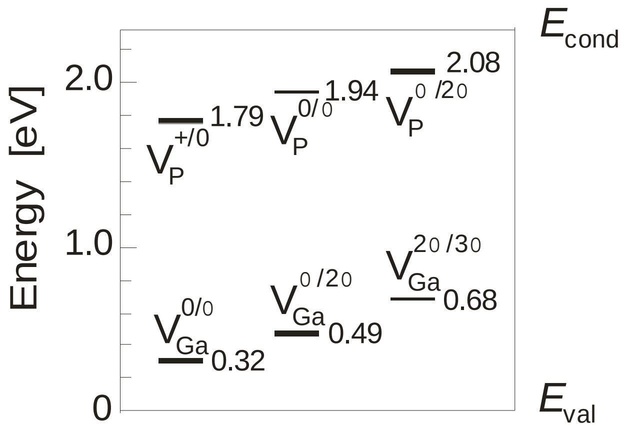
Doppler Coincidence Experiments

- DBCS was used to study the chemical environment of the detected mono-vacancy
- surprise: although complete trapping -> high-momentum Doppler spectrum close to reference sample
- comparison with theoretically calculated spectra required



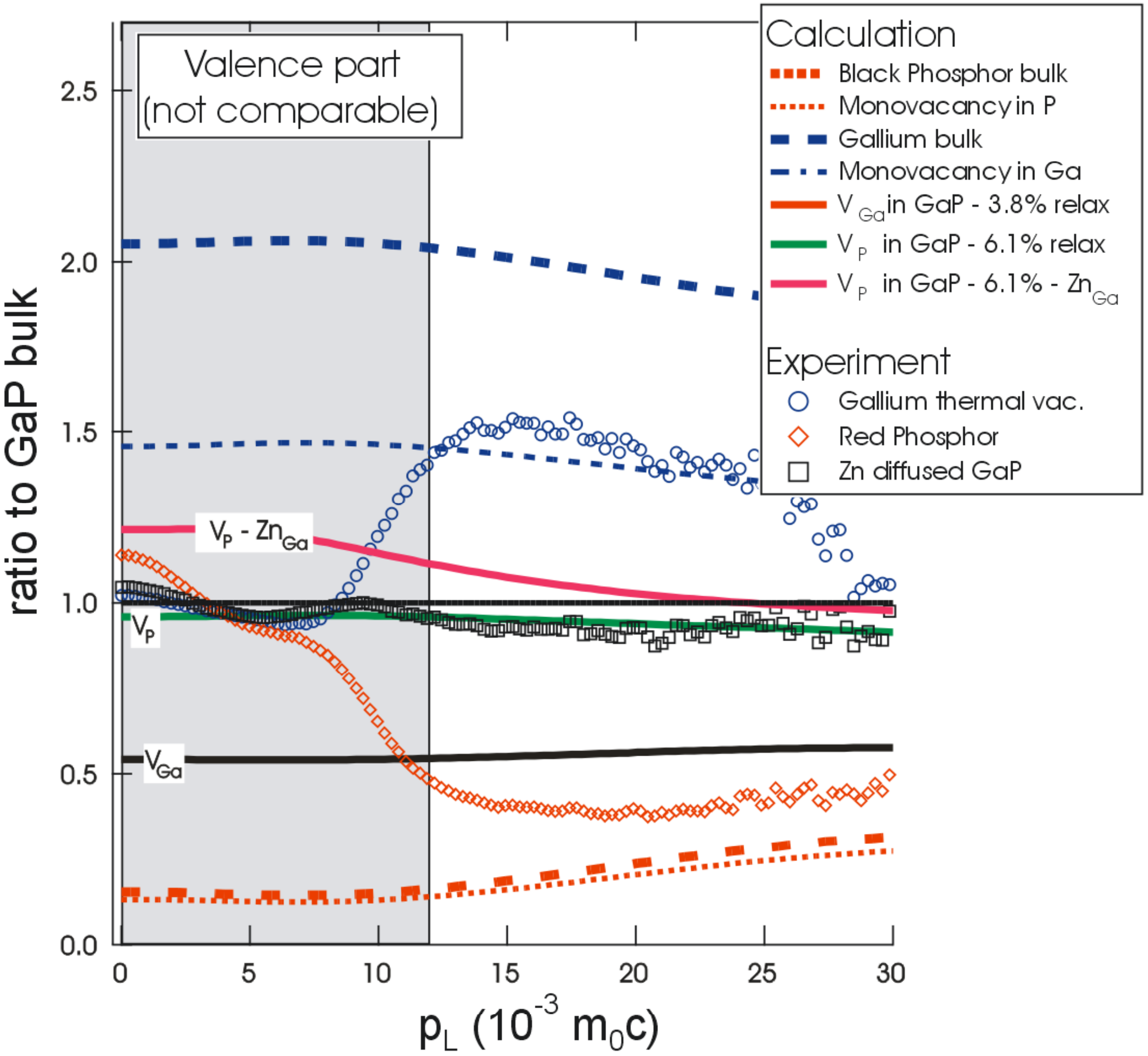
Doppler Coincidence Experiments

- calculations agree well for Ga and P
- V_{Ga} is close to P data, while V_P is very close to the bulk behavior
- conclusion: we detected V_P



(M. Puska, J. Phys. Cond. Mat. 1989)

- however: V_P should be positive in p-type GaP
- we detect probably V_P-Zn_{Ga}

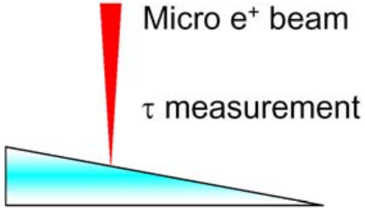


GaP:Zn - Conclusions

- During Zn in-diffusion: vacancies are formed
- concentration is much higher than thermal vacancies
- Vacancy is located in P sublattice
- V_p should be positive -> thus a defect complex is most probably observed
- best candidate: V_P-Zn_{Ga}

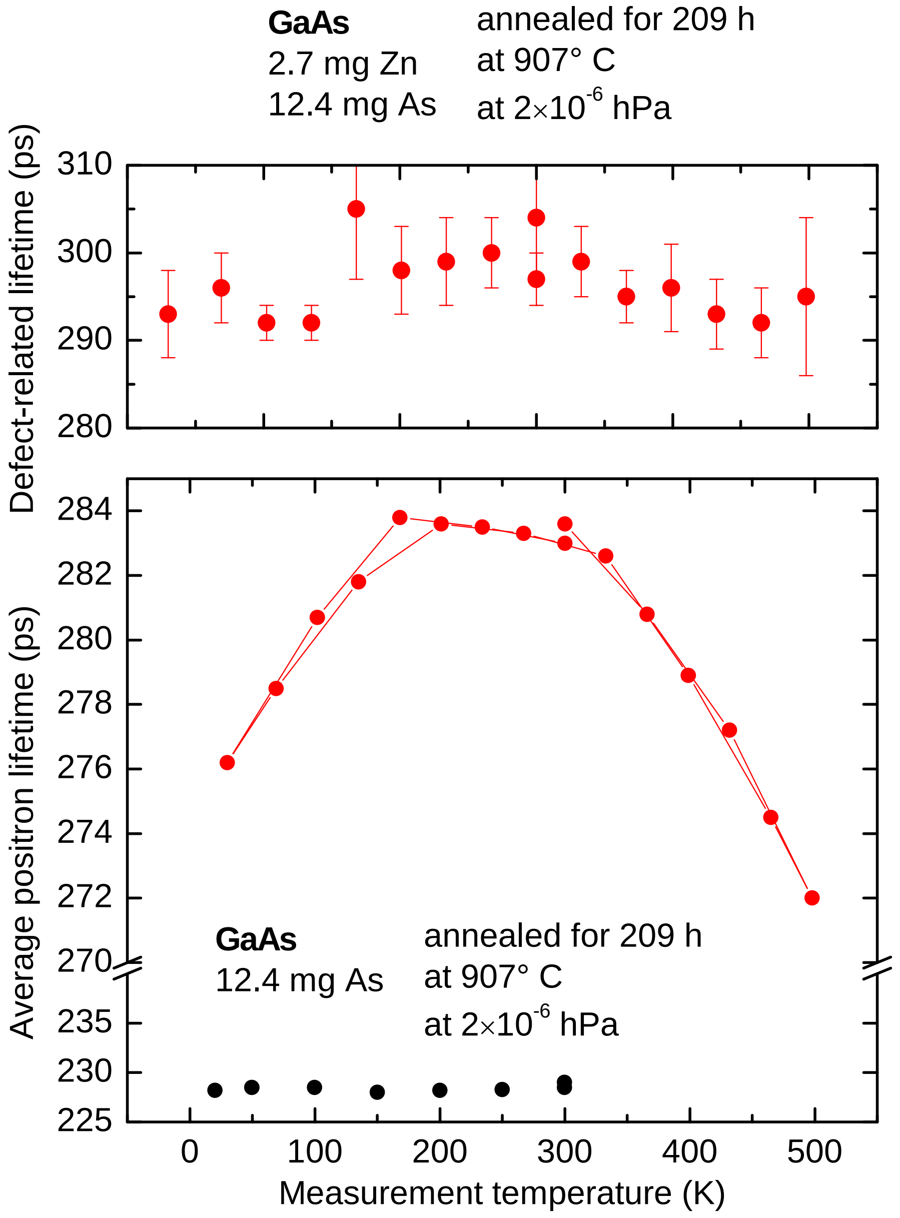
planned experiment:

- comparison of vacancy depth profile with Zn-diffusion profile
- we will use Munich Microbeam and the beveled SIMS samples



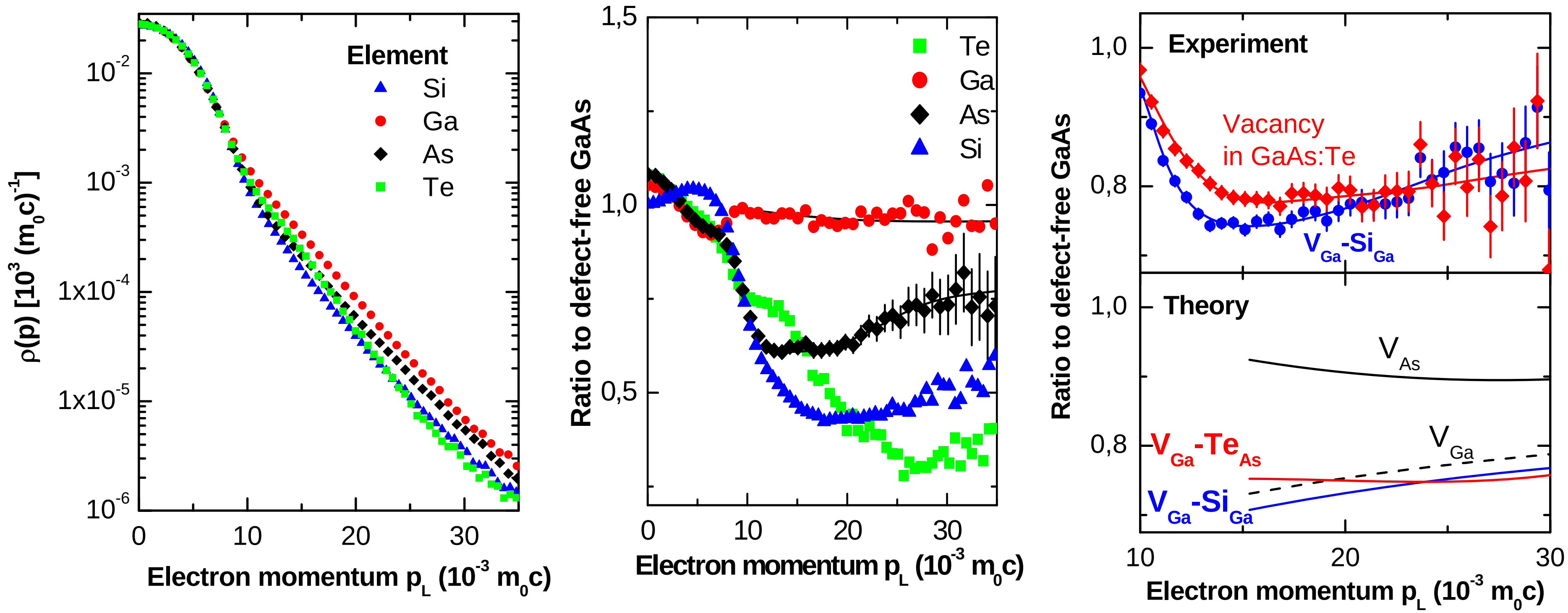
Zn-diffussion in GaAs

- During Zn in-diffusion: vacancies are formed
- Effect is rather strong
- almost saturated positron trapping: [V] > 10^{18} cm^{-3}
- 295 ps seems to indicate V_{As} rather than V_{Ga}



Doppler-Koinzidenz-Spektroskopie in GaAs

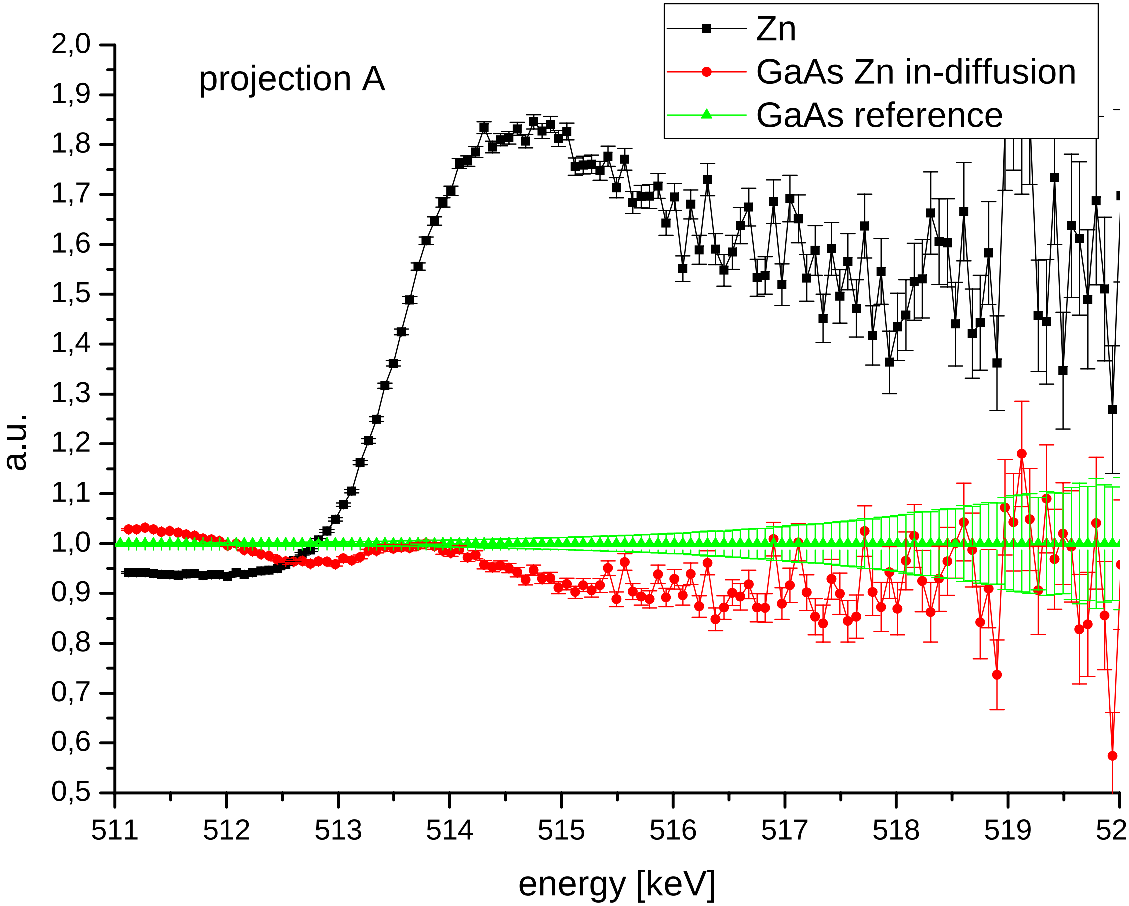
- chemische Sensitivität bei hohen Elektronenimpulsen (Core-Elektronen)
- ein einzelnes Fremdatom in direkter Umgebung einer Leerstelle ist nachweisbar
- Beispiel: V_{Ga}-Te_{As} in GaAs:Te



J. Gebauer et al., Phys. Rev. B **60** (1999) 1464

GaAs:Zn – Doppler Coincidence Spectroscopy

- we performed CDBS measurements at NEPOMUC (FRM-II)
- results need comparison with theoretically calculated spectra



Cu-Diffusion in GaAs

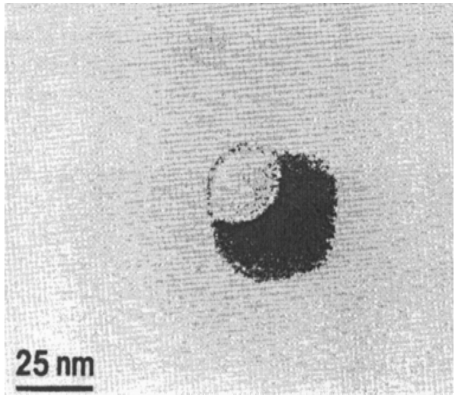
- Copper is an unintentional impurity in most semiconductors
- Cu diffuses rapidly already at low temperatures
- GaAs: diffusion coefficient D = 1.1×10^{-5} cm^2 s^{-1} at 500°C [1]
- Cu diffuses very fast by interstitial diffusion (kick-out process) [2]
- The solubility between 2×10^{16} cm^{-3} (500°C) and 7×10^{18} cm^{-3} (1100°C) [1]
- Cu_{Ga} is a double acceptor
- our work: comprehensive positron annihilation study of GaAs after Cu in-diffusion
- Experimental finding: Vacancy clusters decorated with copper will be formed during annealing of GaAs when Cu is introduced by diffusion before.

[1] R.N. Hall and J.H. Racette, J. Appl. Phys. 35 (1964) 379.

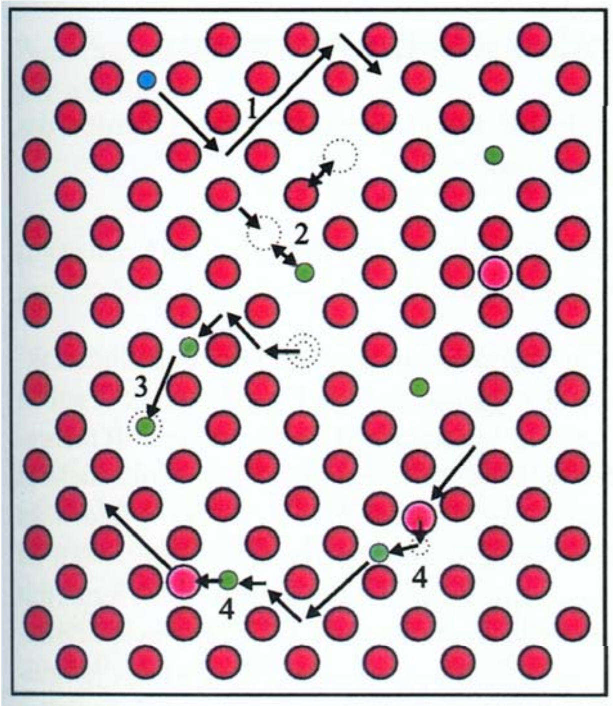
[2] F.C. Frank and D. Turnball, Phys. Rev. 104 (1956) 617.

Literaturergebnisse an GaAs:Zn

- Zn diffundiert via Kick-out Mechanismus
- verdrängt am Ende Ga-Atom: Überschuss an Ga_i
- diese Ga-Atome bilden Zusatzebenen (Interstitial-Loops)
- dafür sind ebenso viele As-Atome nötig
- kommen aus Gitter, hinterlassen As-Leerstellen
- diese As-Leerstellen bilden Leerstellenagglomerate
- dabei kondensiert überschüssiges Ga zu „flüssigem“ Tropfen in Leerstellencluster



M. Luysberg et al., Mat. Sci. & Eng. B13 (1992) 137-151



1. direkter Zwischengitter-mechanismus
2. Leerstellenmechanismus
3. Frank-Turnbull-Mechanismus
4. Kick-out-Mechanismus

Literaturergebnisse an GaAs:Zn

- Modellvorstellung der Bildung von V_{As}-Clustern

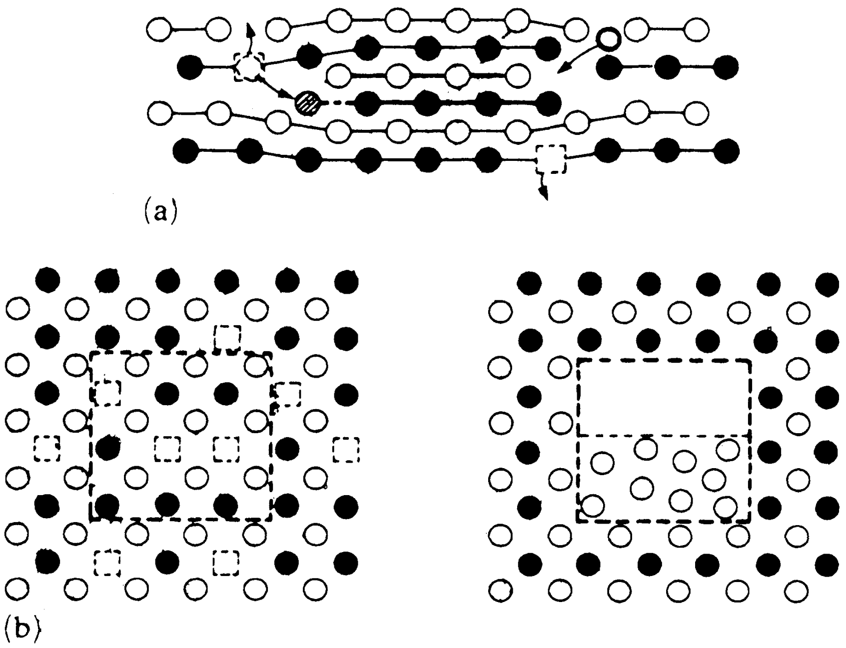
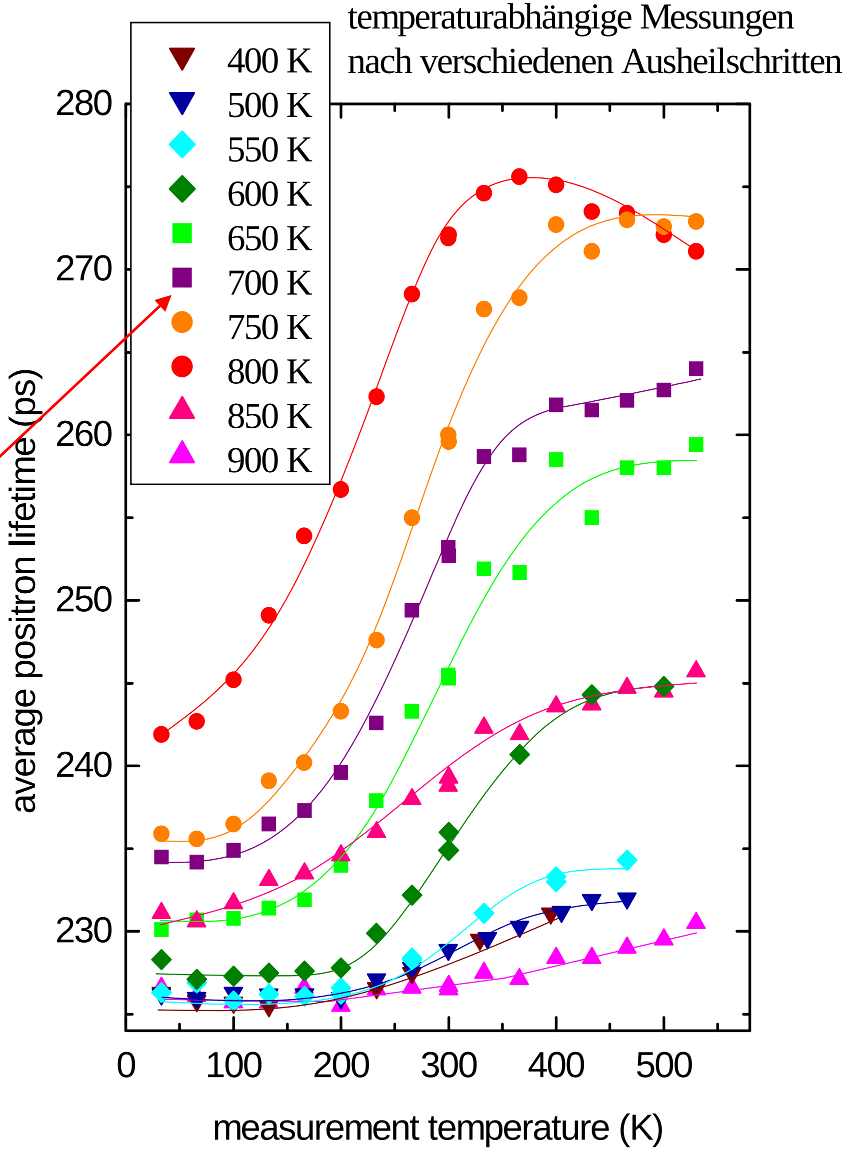


Fig. 12. Model for defect formation in the front region (○, gallium atoms; ●, arsenic atoms): (a) the supersaturation of I_{Ga} (○) caused by the incorporation of zinc atoms results in the formation of perfect interstitial dislocation loops; stoichiometry is preserved by emission of V_{As} (□) at the periphery of growing loops; (b) mobile V_{As} (□) agglomerate and finally collapse into voids by occupying all arsenic lattice sites; the voids are half-filled with gallium (○) and may be filled with further gallium atoms produced by the interstitial–substitutional exchange of zinc.

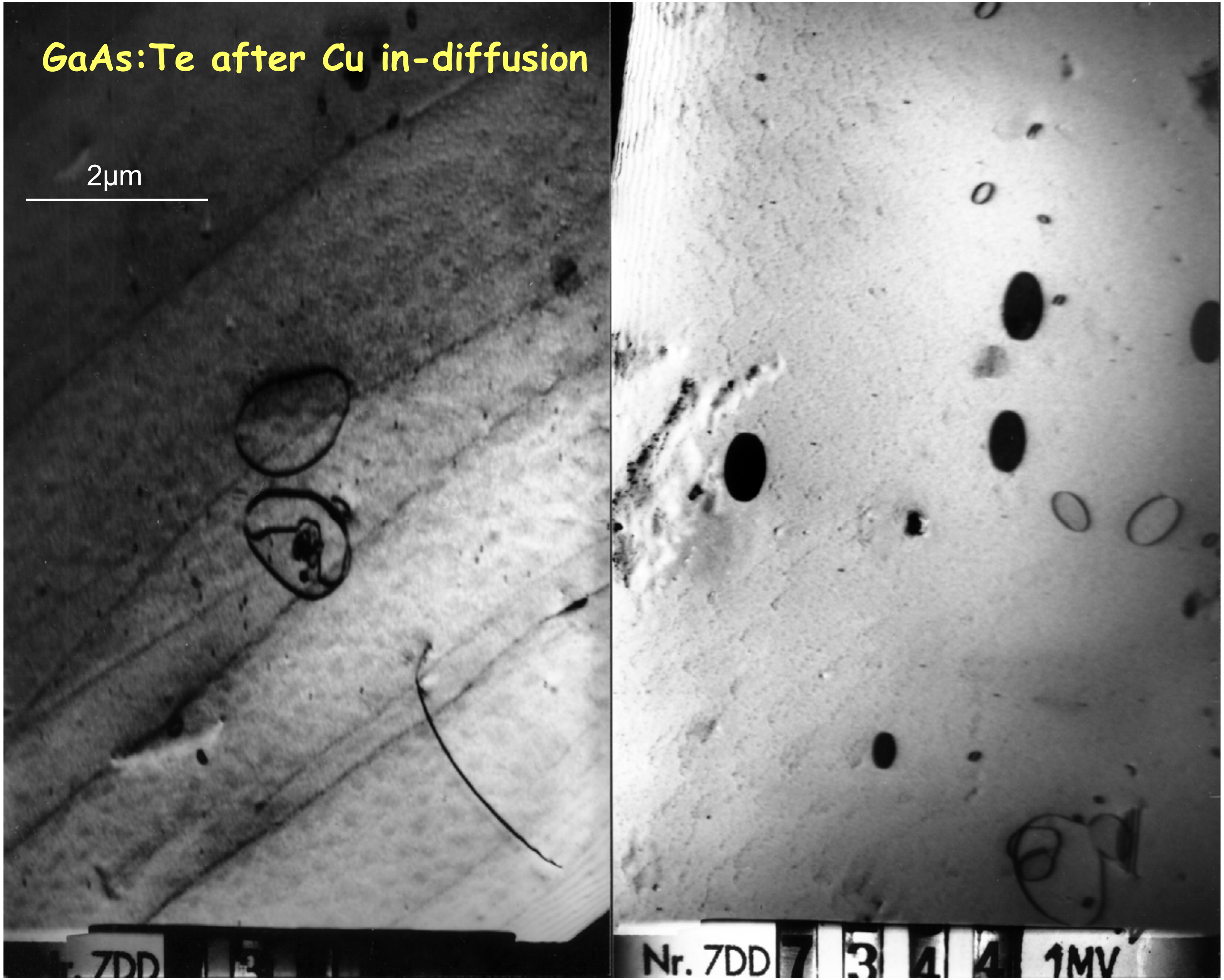
GaAs:Cu

- auch in GaAs:Cu haben wir sowohl die Interstitial Loops als auch Leerstellenagglomerate gefunden (Kooperation Dr. Leipner)
- Vermutung: ähnliche Verhältnisse wie bei Zn-Diffusion
- Experiment mit Positronen:
  1. 30 nm Cu-Schicht aufgedampft
  2. Temperung bei 1100°C (unter As-Druck)
  3. Abschrecken zu RT
  4. Anlassen zu verschiedenen Temp.
  5. Positronenmessung
- Cu ist bei RT übersättigt, beginnt Ausscheidung
- Ergebnis der PAS: Bildung von leerstellenartigen Defekten bei erneuter Cu-Diffusion

GaAs undot. mit 6e18 Cu; abgeschreckt



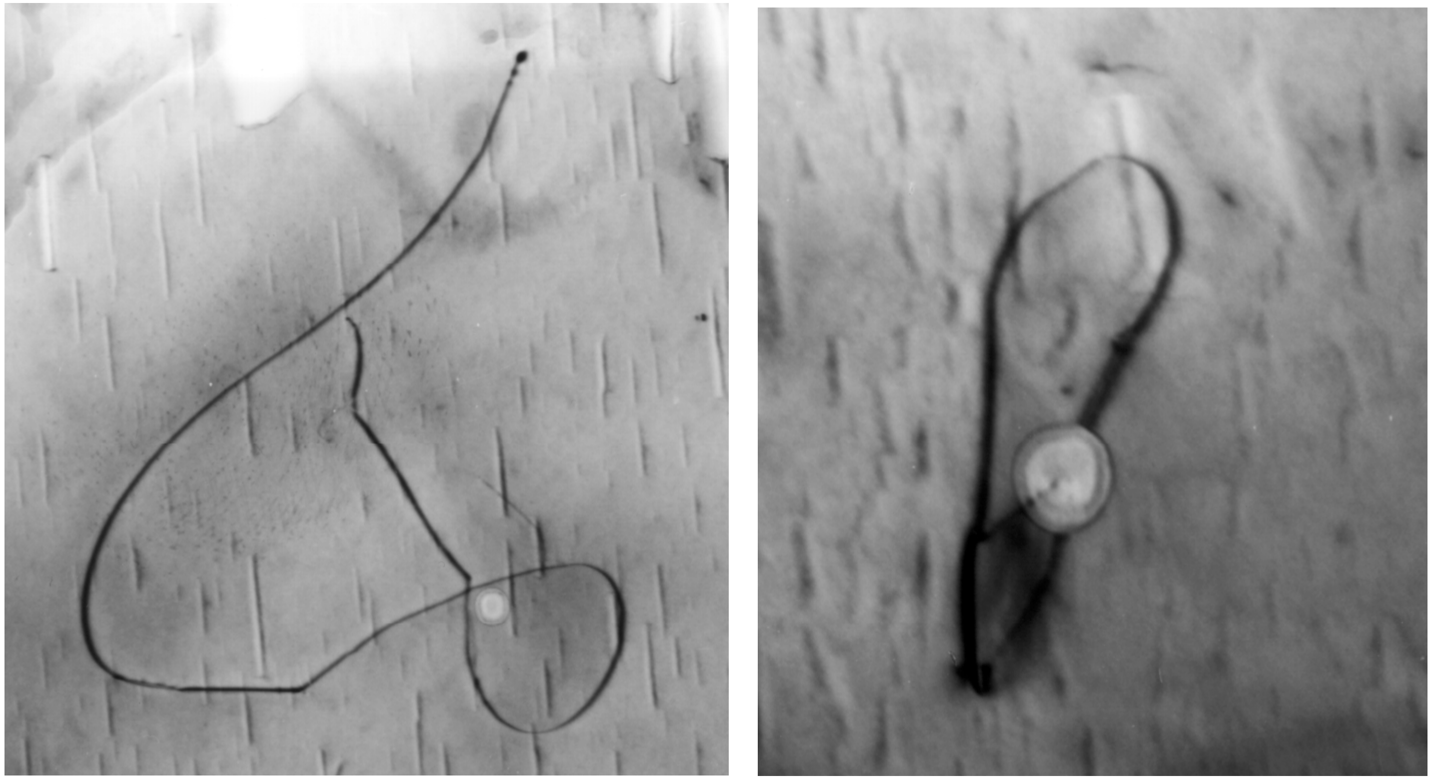
GaAs:Te after Cu in-diffusion



Leipner (1999)

Leerstellencluster in Cu-diffundiertem GaAs:Te

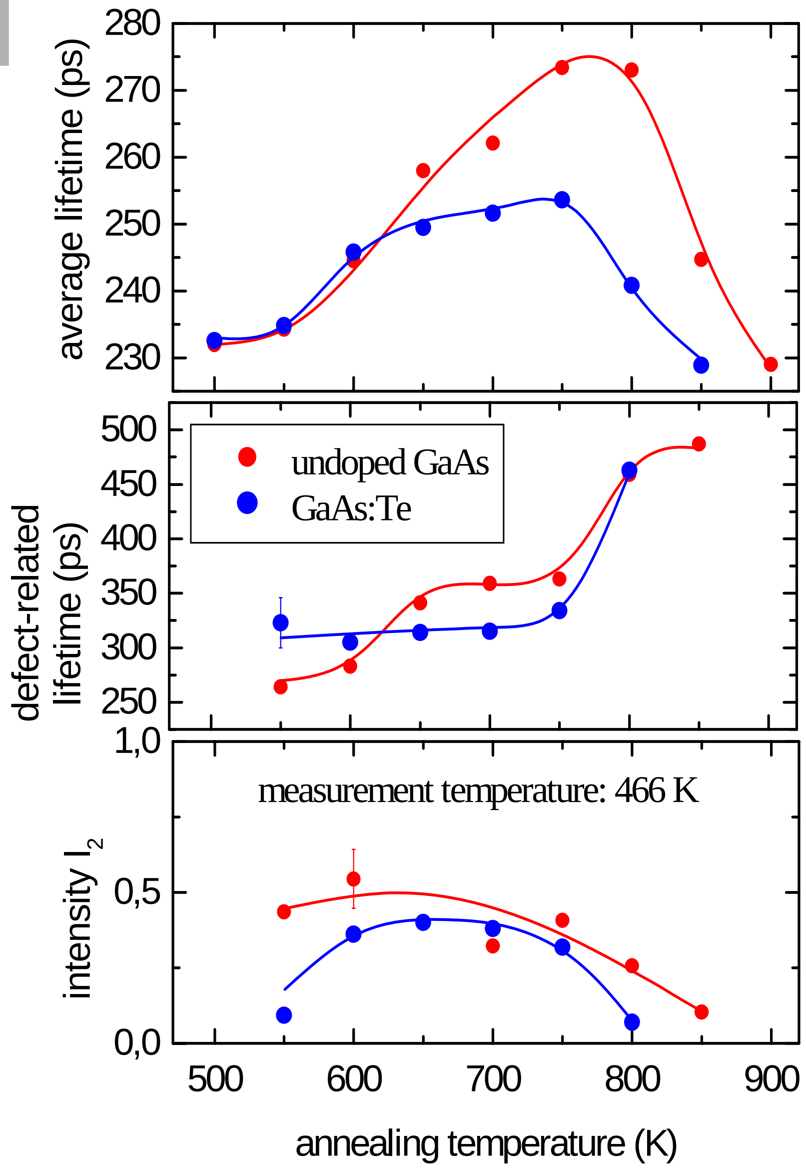
- Probenzustand: GaAs:Te; 30 nm Cu-Schicht (entspricht 5E17 cm^{-3}); bei 600 K getempert nach Abschrecken von 1100°C zu RT
- Leerstellencluster im TEM: Durchmesser ca. 100 nm



(Aufnahmen: Leipner 1999)

Bestimmung des Defekttyps

- Bildung dieser Cluster ist unabhängig von n-Dotierung (Te)
- zunächst ist LD bei ca. 250 ps (Einzelvakanz)
- bei Temperung wird LD größer: 320-350 ps entspricht etwa Doppelvakanz
- bei 800 K: $\tau_2 > 450$ ps: große Leerstellen-Agglomerate (n > 10)



Zusammenfassung

- Bei Cu-Diffusion entstehen Leerstellen und Leerstellen-Agglomerate, die mit Cu dekoriert sind
- sind relativ klein (n = 1 … 10 bei Temperung unter 800 K)
- mit TEM zusätzlich: sehr große Leerstellencluster (100 nm Durchmesser)
- zusätzliche Untersuchungen (Positronen, Hall-Messungen, TEM, SIMS, SAXS)
    - Bilden sich große Cluster bereits beim Abkühlen?
    - Theoretische Rechnungen: Wie viel Cu-Atome sind an Cluster?
    - Wie verhält sich Cu in anderen III-V-Verbindungen?
    - Bilden andere „Kick-out“-Elemente ebenfalls kleine Leerstellencluster-Fremdatom-Paare?
    - Wie wirken sich diese Defekte auf die Diffusionsmechanismen aus?