FORMATION AND DISSOCIATION MECHANISMS OF H (D)-DOPANT COMPLEXES IN MID AND WIDE BAND GAP SEMICONDUCTORS

by

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GaN (E_g=3.39 eV, direct gap, wurtzite structure)

Growth techniques: MOCVD, GSMBE, MBE

Applications in optoelectronics (blue and UV), high power and high frequency electronics, photodetectors.

ZnO (E_g=3.37 eV, direct gap, wurtzite structure)

Growth techniques: MOCVD, MBE, CSVT

Applications in LEDs and lasers (blue and UV), conductive transparent windows for solar cells, surface acoustic wave systems.

Diamond (E_g=5.47 eV, indirect gap, f.c.c. structure)

Growth technique: microwave plasma CVD from a CH_4/H_2 mixture

Applications in high power, high frequency and high temperature electronics, UV detectors, electrochemistry, surface acoustic wave systems (combined with ZnO) etc ...





INTRODUCTION

Wide band gap semiconductors are often grown by techniques where native hydrogen is generated and is incorporated in the semiconductor during the growth.

ex: GaN:Mg grown by MOCVD

ex: ZnSe:N grown by GSMBE



In addition, several processing steps may introduce hydrogen during the device fabrication (RIE, chemical etching etc ...).





- Introduction.
- Mg-H complexes in GaN.
- General theory of hydrogen in semiconductors and the particular case of ZnO.
- Interactions between hydrogen and boron acceptors in diamond.
- Dissociation mechanism of D-dopant complexes in diamond under e-beam irradiation.
- Comparison with the dissociation mechanism of Si-H(D) complexes in GaAs.
- Conclusions.





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INTERACTIONS BETWEEN HYDROGEN AND MAGNESIUM IN GaN

(Götz et al, APL 69, 3725, 1996)





Under hydrogenation (deuteration), the resistivity increases and LVM of H (D) are detected



ATOMIC STRUCTURE OF (Mg,H) COMPLEXES IN GaN



 $v_{\rm H}$ =3125 cm⁻¹

(Neugebauer et al, Hydrogen in Semiconductors II, Semiconductors and Semimetals, vol.61, 1999)





FORMATION ENERGY AND ELECTRONIC STATES OF HYDROGEN IN GaN

Under thermodynamic equilibrium: $C = N_{sites} \exp[-E_f/kT]$



H+ is the most stable species in p-type $GaN \Rightarrow H$ is a donor in p-type GaN



(Neugebauer et al, PRL 75, 4452, 1995)



FORMATION MECHANISM OF THE (Mg,H) PAIRS IN GaN DURING THE GROWTH PROCESS

It is the result of a two step process:

2) Compensation of the free holes by the hydrogen donors:



2) Coulombic attraction between the ionized acceptors and the protons:

Mg-+H+ \Rightarrow (Mg,H) E_{diss} (Mg,H) = 2.03 eV

This mechanism holds true for a number of semiconductors: Si, GaAs, ZnSe etc ...





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GENERAL THEORY OF HYDROGEN IN SEMICONDUCTORS

Calculations of:

- the valence band offsets for unstrained systems.
- the position of the H+/- levels with respect of the valence band maximum.



 \Rightarrow Universal alignment of the hydrogen levels

(C.Van de Walle, Physica B, 376-377, 1, 2006)





THE PARTICULAR CASE OF ZnO

As-grown ZnO is always n-type BUT the origin of the donors is not clear.

Theory: Interstitial H⁺ has the lowest formation energy for all the Fermi level positions.

(Van de Walle et al, PRL, 2001)

Experimentally:

- In ZnO, hydrogen is a shallow donor:
 - EPR: E_d=35 ±5 meV (*Hofmann et al, PRL, 2002*)
 - HREELS: E_d=25 meV (*Qiu et al, PRL, 2008*)

Both theory and experiments conclude that H is a shallow donor in ZnO.







Vibrational signatures of hydrogen-related defects in ZnO

	LVM (cm-1)	Defect	Reference	
ZnO	2004	⁶⁴ Zn-H	Nickel APL 87 (2005) 211905	
	3191.6	Cu-H	Lavrov Physica B 340 (2003) 195	
	3312.2	Complexe V _{Zn} +2H	Lavrov Physica B 340 (2003) 195	
	3349.6	Complexe V _{zn} +2H	Lavrov Physica B 340 (2003) 195	
	3326	H _{AB}	Jokela Physica B 401 (2007) 395	
		V _{za} H-	Lavrov Physica B 401 (2007) 366	An
	3347	Cu-H ₂	Lavrov Physica B 401 (2007) 366	│ ↑
	3374	Cu-H ₂	Lavrov Physica B 401 (2007) 366	
	3577	Ni-H	Lavrov Physica B 340 (2003) 195	
	3611.3	H _{BC}	Lavrov Physica B 340 (2003) 195	
ZnO:N	3150	N-H	Jokela PRB 76 (2007) 193201	Bo





c-axis

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ELECTRONIC STATES OF HYDROGEN IN DIAMOND

(Goss et al, PRB, 2002)

c.b.



A small energy window exists for the Fermi level where H⁰ is the most stable species.

H+ is the most stable species in p-type diamond.





DIFFUSION MECHANISM OF HYDROGEN IN BORON-DOPED DIAMOND



(Chevallier, Thin film diamond II, Semiconductors and Semimetals, vol. 77, 2004)





Influence of the complex formation on the electrical properties of boron-doped diamond

(Saguy et al, DRM 10, 453, 2001)

(Hall effect and conductivity measurements)



At 300 K, p decreases by a factor of 60 while μ_p increases by a factor of 6





Influence of the complex formation on the optical properties of boron-doped diamond





Conclusion: the B-D complex formation induces a removal of the boron acceptor states



THE (B,H) COMPLEXES IN DIAMOND

Formation process during diffusion

Atomic structure



 $B^- + H^+ \longrightarrow (B,H)^o$

LVM signatures

Theory: 2657 cm⁻¹ and 1965 cm⁻¹ No experimental data

Thermal dissociation energy of B-H complexes

 $E_{diss} = 2.5 \text{ eV}$ (450°C, 1h \Rightarrow 90% dissociation)



 $E_{migration}(H^+)$ (th.)=0.1-0.2 eV



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What happens to B-D complexes in diamond under an e-beam irradiation ?



Most of the boron acceptors in the e-beam area have been reactivated

 \Rightarrow The e-beam induces a dissociation of the B-D complexes



Next step: follow the dissociation kinetics as a function of I_{beam}



Influence of the e-beam current on the dissociation yield

x10¹⁸ REACTIVATED BORON(cm⁻³) BD, T=102K I=25 nA Dissociation yield η : I=10 nA 2 nA: not measurable 10 nA: 5.6×10^{-8} /electron 25 nA: 7.4x10⁻⁷/electron (J.Barjon et al, APL 89, 232111, 2006) I=2 nA 2 x10²¹ 1 $\mathbf{0}$ ELECTRON DOSE (cm⁻²)

The reactivated boron concentration is deduced from a calibration curve $N_a = K(T) I_{BE}/I_{FE}$.

 \Rightarrow the dissociation yield η strongly depends on the current





POSSIBLE DISSOCIATION MECHANISMS

- 1) Direct electronic excitation ? (Menzel and Gomer model)
- η independent of the current
 η independent of the temperature

OR

2) Multiple vibrational excitation ?

(Local vibrational excitation of the B-D bond due to inelastic e⁻ interaction)

- η dependent on the current
- η dependent on the temperature





Our results support a multiple vibrational excitation mechanism

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Si-H complexes in GaAs excited by UV or an electron beam irradiation: a case of dissociation mechanism by electronic excitation (1)

GaAs epilayers with Si-H or Si-D complexes excited by illumination



(Loridant-Bernard et al, APL, 1998)





Si-H complexes in GaAs excited by UV or an electron beam irradiation: a case of dissociation mechanism by electronic excitation (2)



(Chevallier et al, APL, 1999)

The dissociation yield is independent of the illumination power density and almost independent of temperature.



Observation of a strong isotope effect in the dissociation efficiency.



CONCLUSIONS

- Modern growth techniques of wide band gap semiconductors may introduce large concentrations of hydrogen.

- This hydrogen passivates dopants as a result of (H-dopant) complex formation.

- Direct proof of the existence of the complexes is given by the observation of local vibrational modes related to hydrogen.

- The origin of the complex formation is the counterdopant character of hydrogen: it is a deep donor in p-type semiconductors while it is a deep acceptor in n-type semiconductors.

- Hydrogen exhibits a peculiar behavior in ZnO: it is a shallow donor \Rightarrow hydrogen participates to the residual n-type conductivity of ZnO.





- In diamond, H (D) passivates boron acceptors as a result of the formation of B-H (D) complexes.
- These complexes are dissociated at T=100 K under electron beam irradiation.
- The dissociation kinetics strongly depends on the current.
- This result supports a multiple vibrational excitation mechanism for B-D complex dissociation in diamond.
- Si-H(D) complexes in GaAs excited by UV or hot electrons dissociate by an electronic excitation mechanism.





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