

**THIRD WORKSHOP ON
THIN FILMS PHYSICS AND TECHNOLOGY
(8 - 24 MARCH 1999)
including
TOPICAL CONFERENCE ON
MICROSTRUCTURE AND SURFACE MORPHOLOGY
EVOLUTION IN THIN FILMS
(24 - 26 MARCH 1999)**

**"H-mediation, surface segregation, ultra-high doping
and their effects on Si and $\text{Si}_{1-x}\text{Ge}_x$ growth kinetics
during GS-MBE and UHV-CVD"**

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***3rd ICTP/IUVSTA Workshop on Thin Film Physics
Trieste, Italy***

**H-Mediation, Surface Segregation, Ultra-High Doping
and their Effects on Si and $\text{Si}_{1-x}\text{Ge}_x$ Growth Kinetics
during GS-MBE and UHV-CVD**

Joe Greene
University of Illinois

Monday, March 22, 8:30 to 10:30

Outline:

1. ALE Si
 - a. Mechanisms
 - b. Modeling
2. GS-MBE/UHV-CVD Si
 - a. Mechanisms
 - b. Modeling
3. B doping
 - a. Incorporation mechanism
 - b. Electronic properties
4. Ultra-high B doping
 - a. Incorporation
 - b. Effect on R_{Si}
 - c. Modeling
 - d. Electronic properties
5. GS-MBE/UHV-CVD $\text{Si}_{1-x}\text{Ge}_x$
 - a. Mechanism
 - b. Modeling
 - c. B doping and electronic properties

Atomic-level Control during Film Growth under Highly Kinetically Constrained Conditions

*** $\text{Si}_{1-x}\text{Ge}_x$ atomic-layer epitaxy (ALE)**

- Low-temperature growth
- δ -doping

*** Effects of H coverage during GS-MBE/UHV-CVD**

- Ultra-high doping vs film growth kinetics
- Minimize Ge segregation during $\text{Si}_{1-x}\text{Ge}_x$ growth

*** Fundamental limits of epitaxy**

- $T_{\text{epi}} \rightarrow t_{\text{epi}}$
- Use of hyperthermal beams
- Metastable phases ($\text{Ge}_{1-x}\text{Sn}_x$, $\text{Ti}_{1-x}\text{Al}_x\text{N}$,)

*** Evolution of surface morphology**

- Kinetic roughening
- Strain-induced roughening/smoothing

*** Evolution of microstructure and texture**

- Hyperthermal beams
- Texture inheritance

Atomic-Layer Epitaxy (ALE)

ALE is a cyclic vapor-phase epitaxial film growth technique which incorporates *self-limiting* kinetic processes which result in the deposition of θ ML per growth cycle where $\theta \leq 1$ ML.

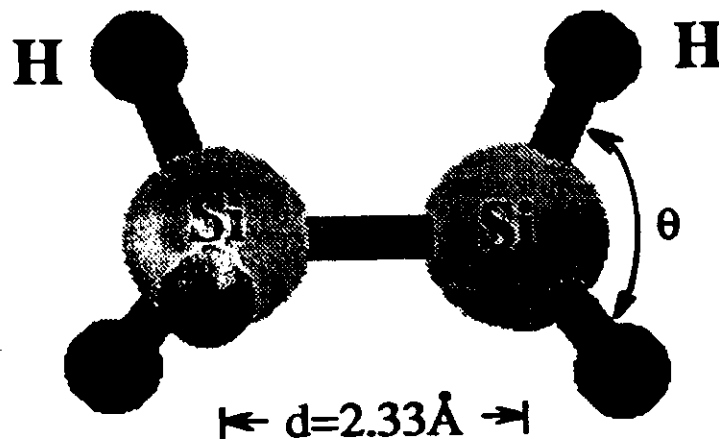
$$\Rightarrow R_{\text{cycle}} = \theta \text{ (ML/cycle)}$$

Advantages:

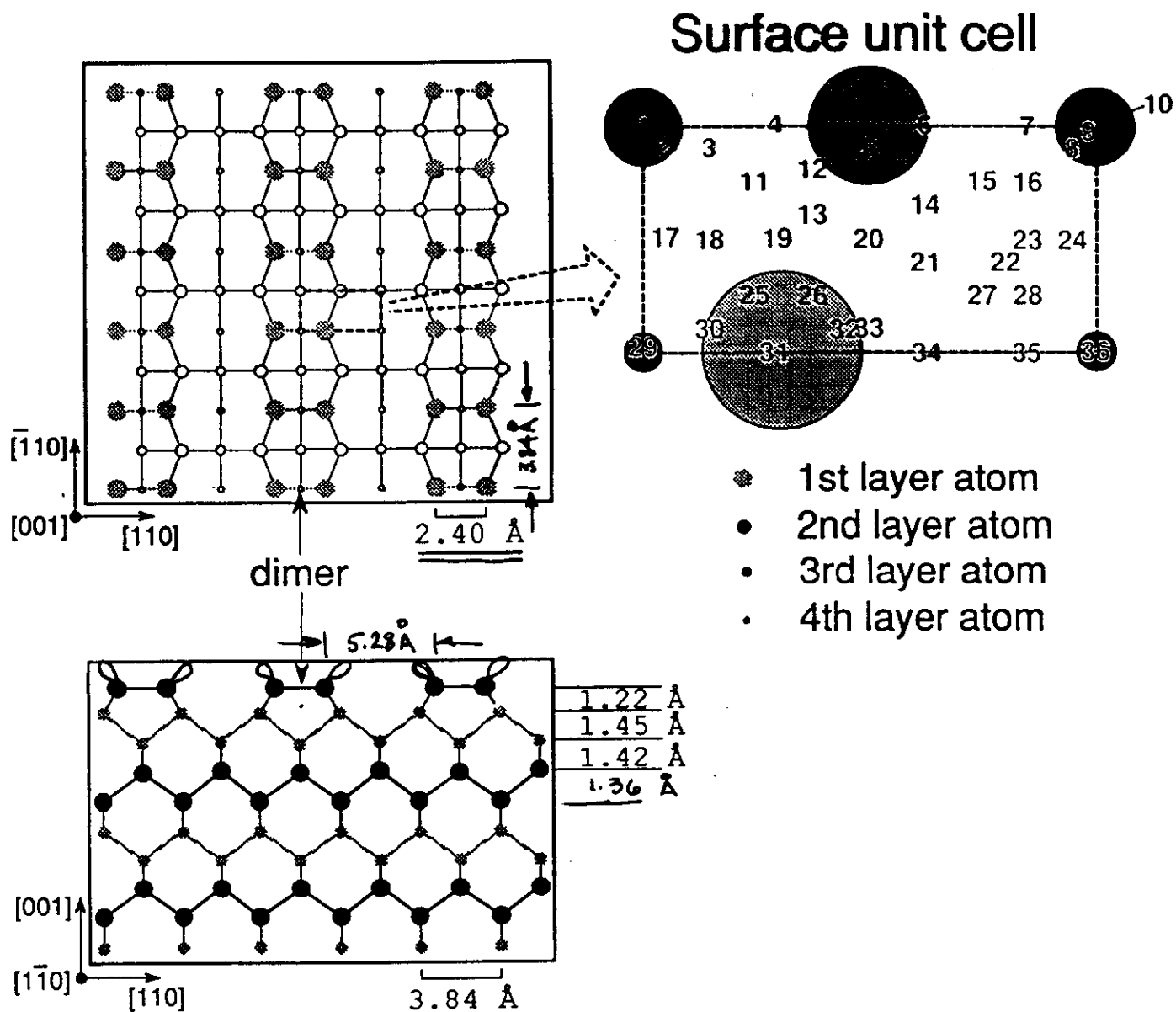
- $R \neq f(T_s, P_{\text{gas}})$; wide process windows
- $\therefore$ overall $E_a = 0$
- $\therefore$ low T_s possible
- Excellent control over film thickness:
 $t = R_{\text{cycle}}(\text{\#cycles})$
- Selective area deposition
- δ -doping
- QW heterostructures
-
-

Precursor for Si ALE: Si_2H_6

- High sticking probability on Si & Ge
 $\sigma(\text{Si}_2\text{H}_6) > 10^4 \times \sigma(\text{SiH}_4)$
- Gas phase dimer $\simeq \text{Si}(001)2\times 1$

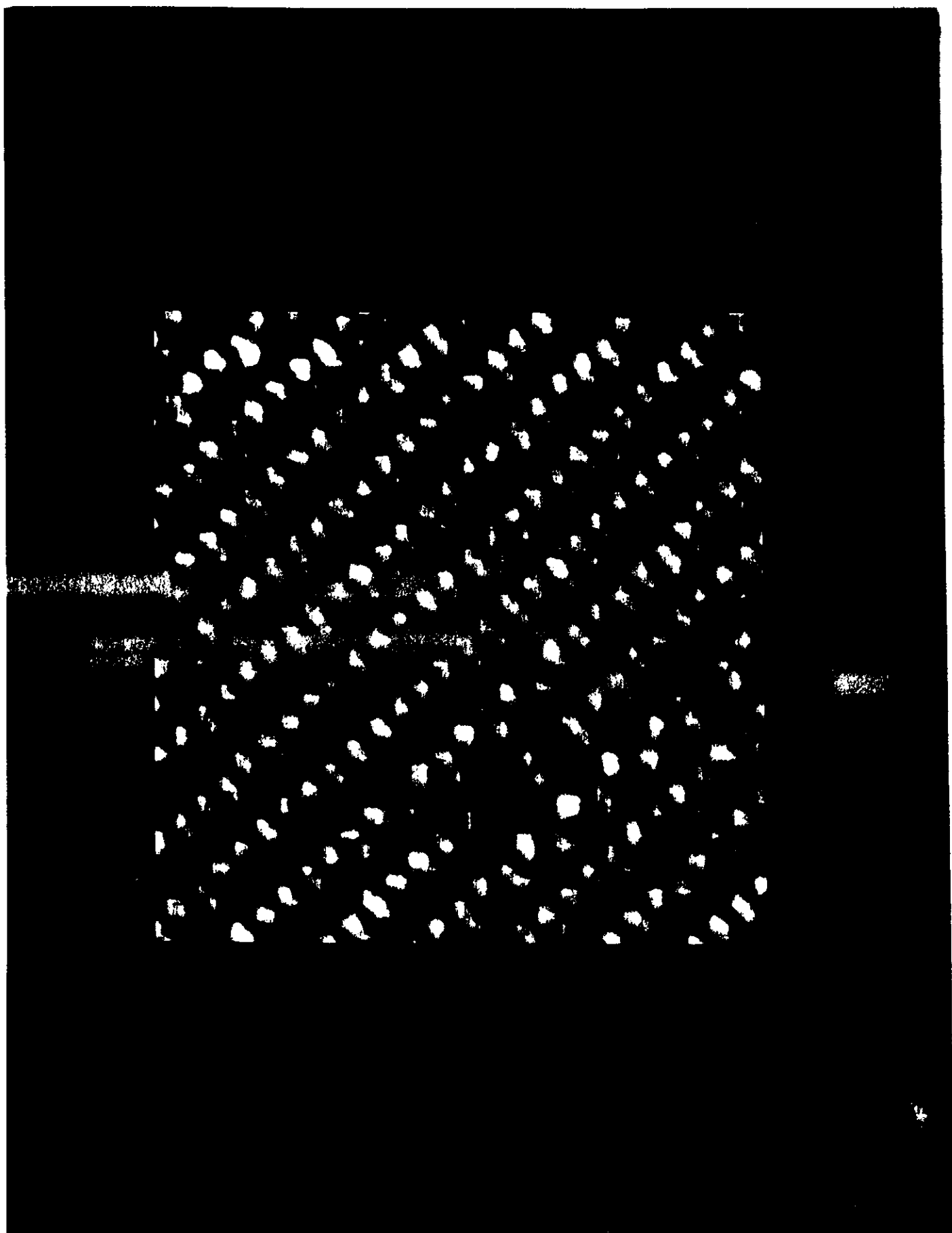


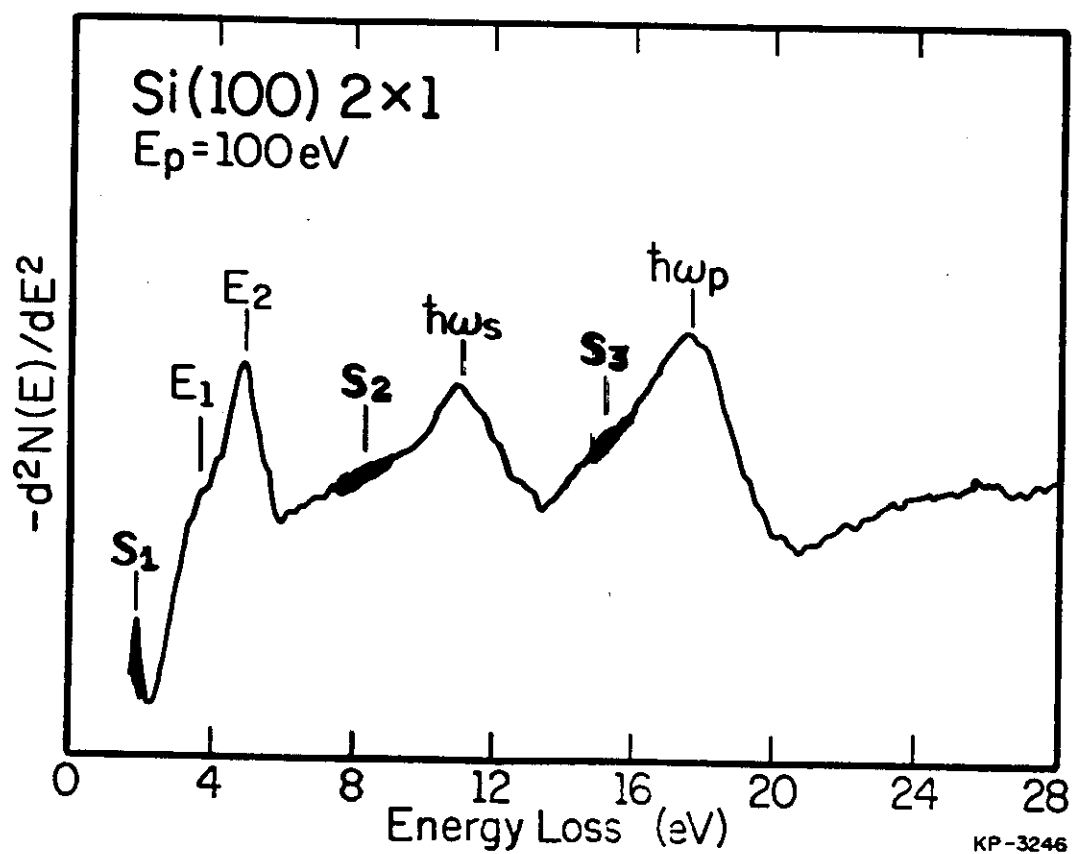
- $E_b(\text{Si-Si}) = 3.3 \text{ eV}$
- $E_b(\text{Si-H}) = 3.8 \text{ eV}$
- $d(\text{Si-Si}) = 2.33 \text{ \AA}$
- $d(\text{Si-H}) = 1.49 \text{ \AA}$
- $\theta(\text{Si-Si-H}) = 110.3^\circ$



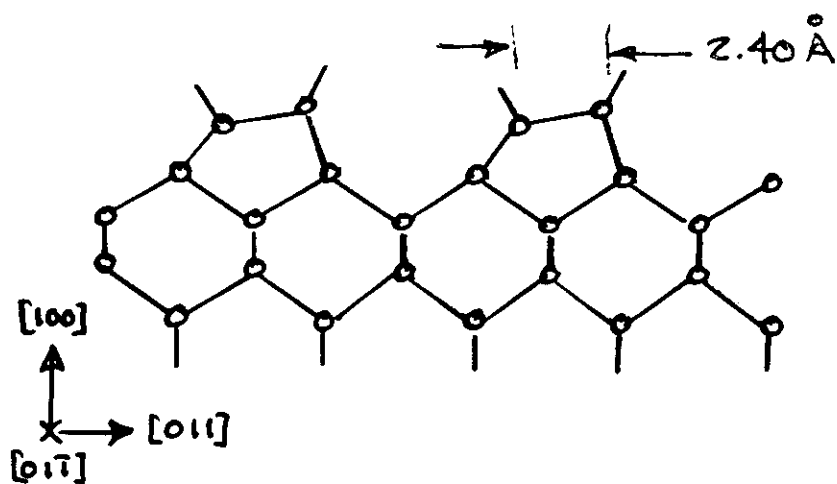
M. Kitabatake and J.E. Greene, J. Appl. Phys.
 73, 3183 (1993).

Fig 1

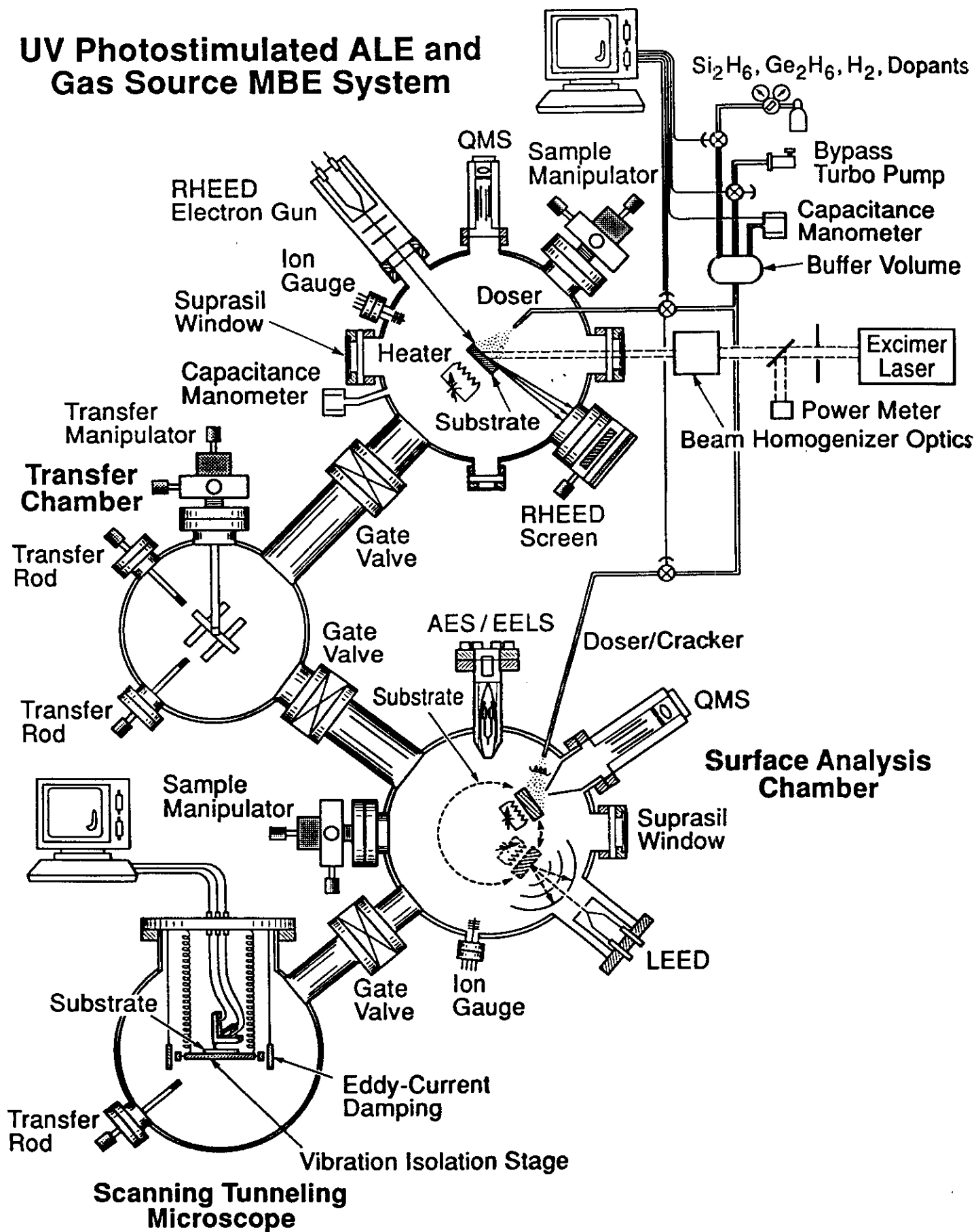




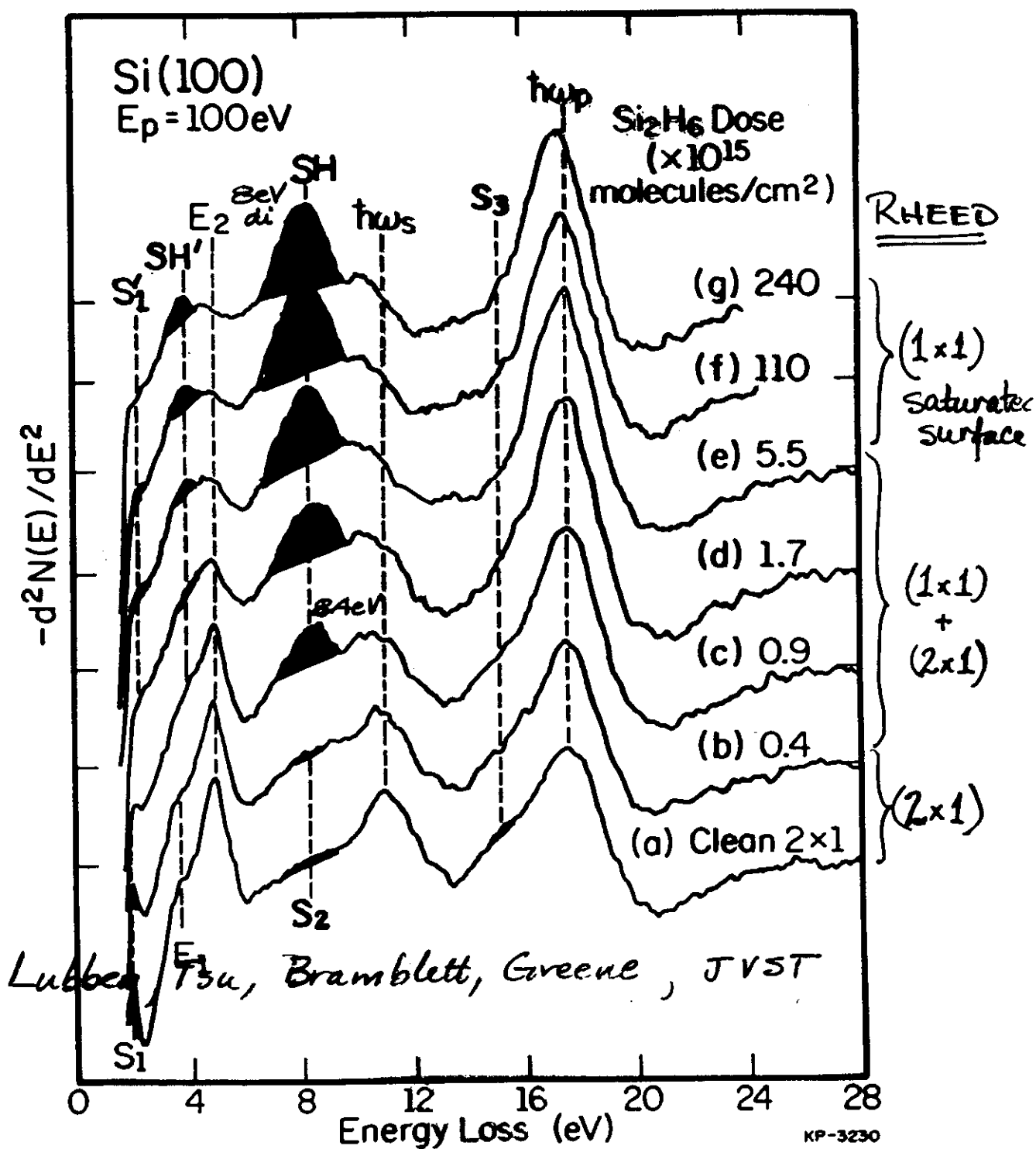
S_1 = surface dangling bond state
 S_2, S_3 = backbond states

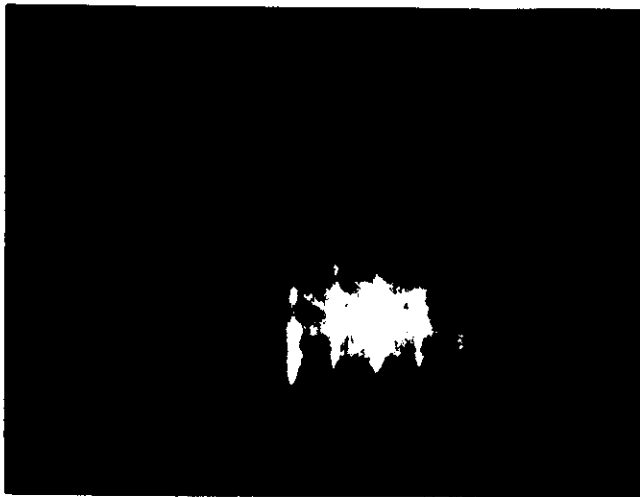


UV Photostimulated ALE and Gas Source MBE System

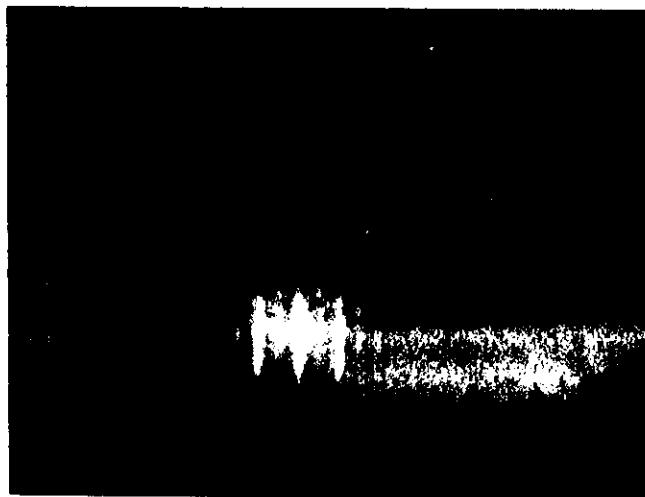


$$T_s = 500 \text{ K}$$

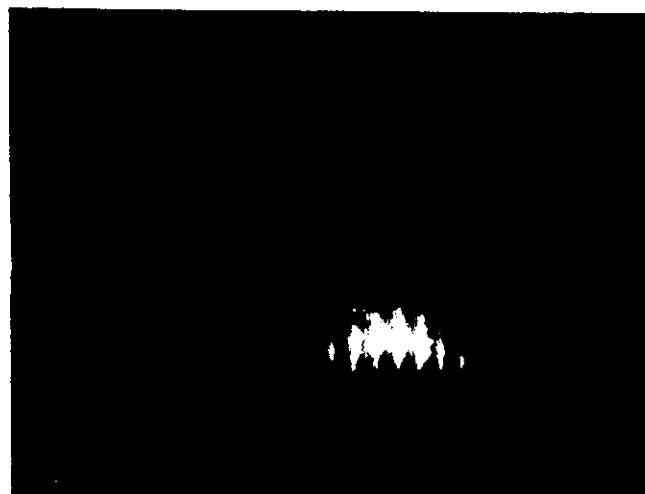




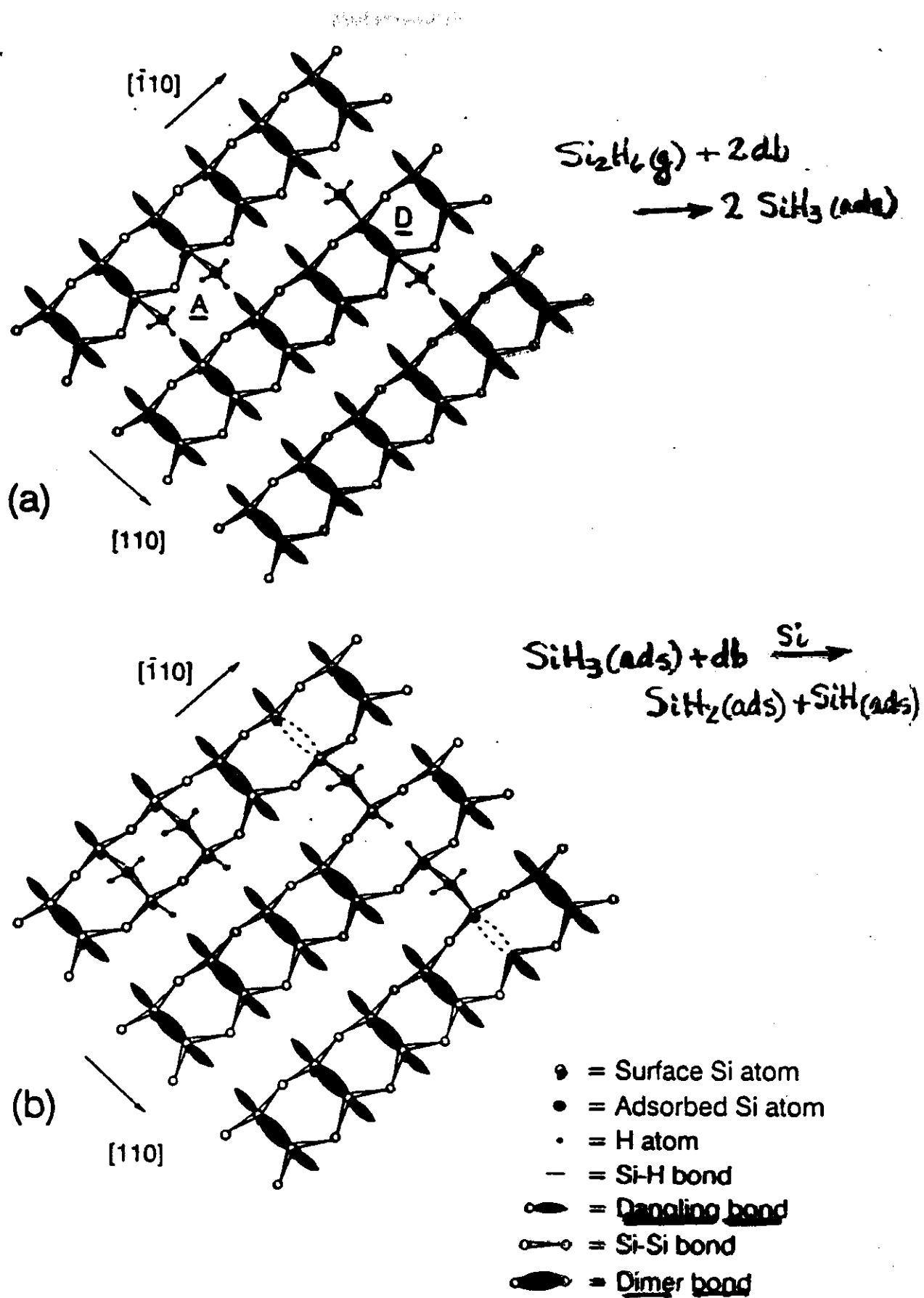
1x1



2x1
+
1x1



2x1



7. Schematic illustration of the Si(001) surface after (a) dissociative chemisorption of Si_2H_6 onto a single dimer (D) and onto adjacent dimers (A), and (b) dissociation of the adsorbed SiH_3 radicals to form SiH_2 and H.

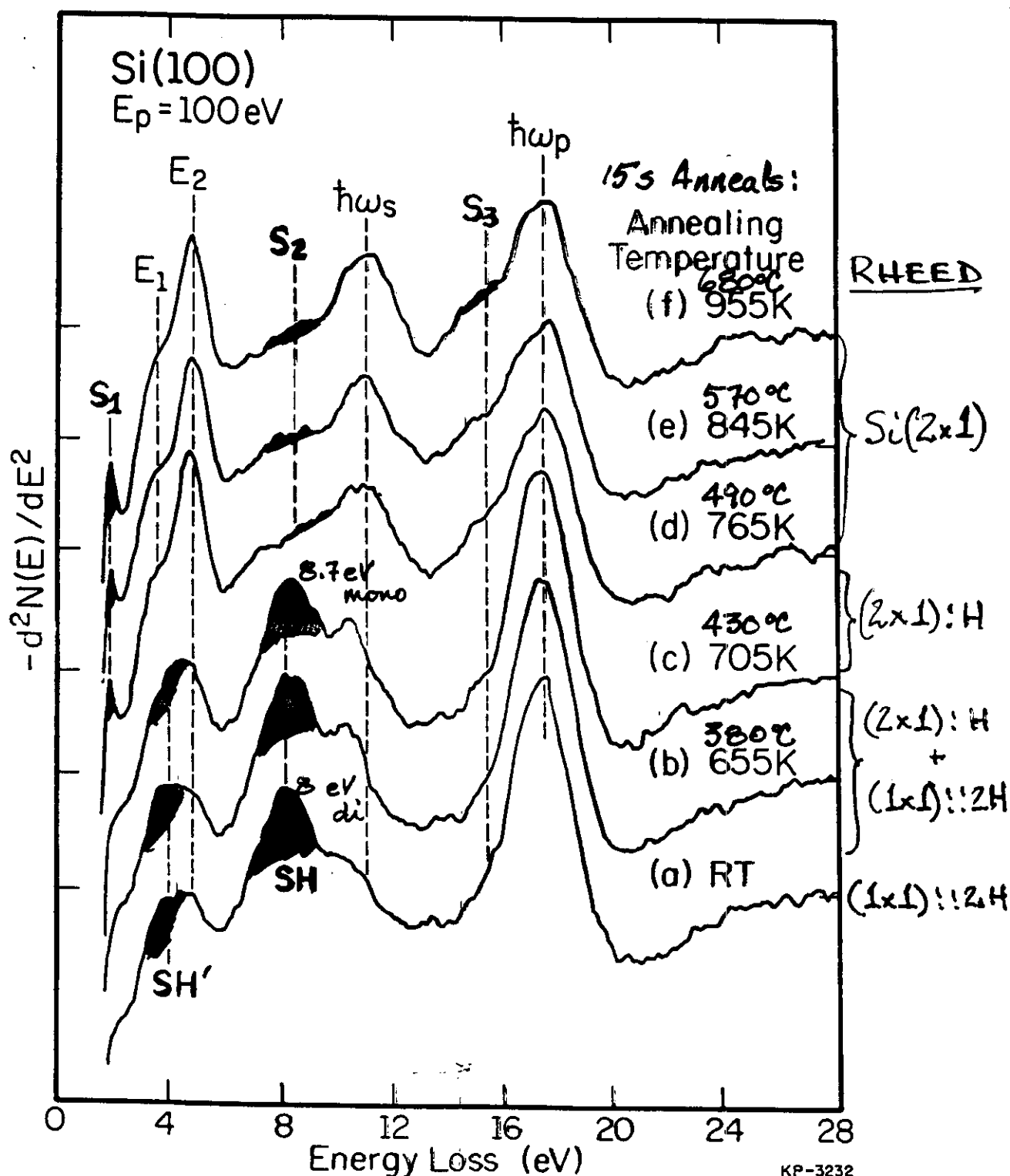
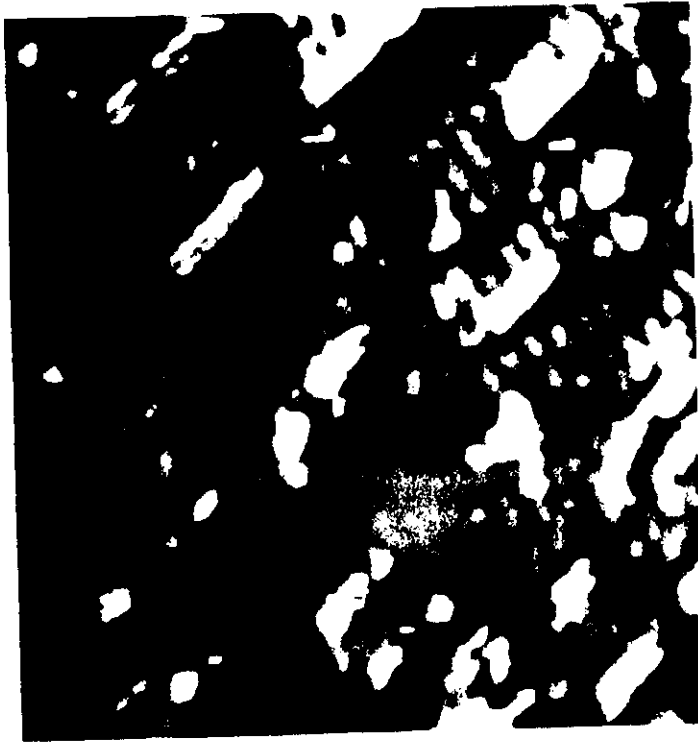


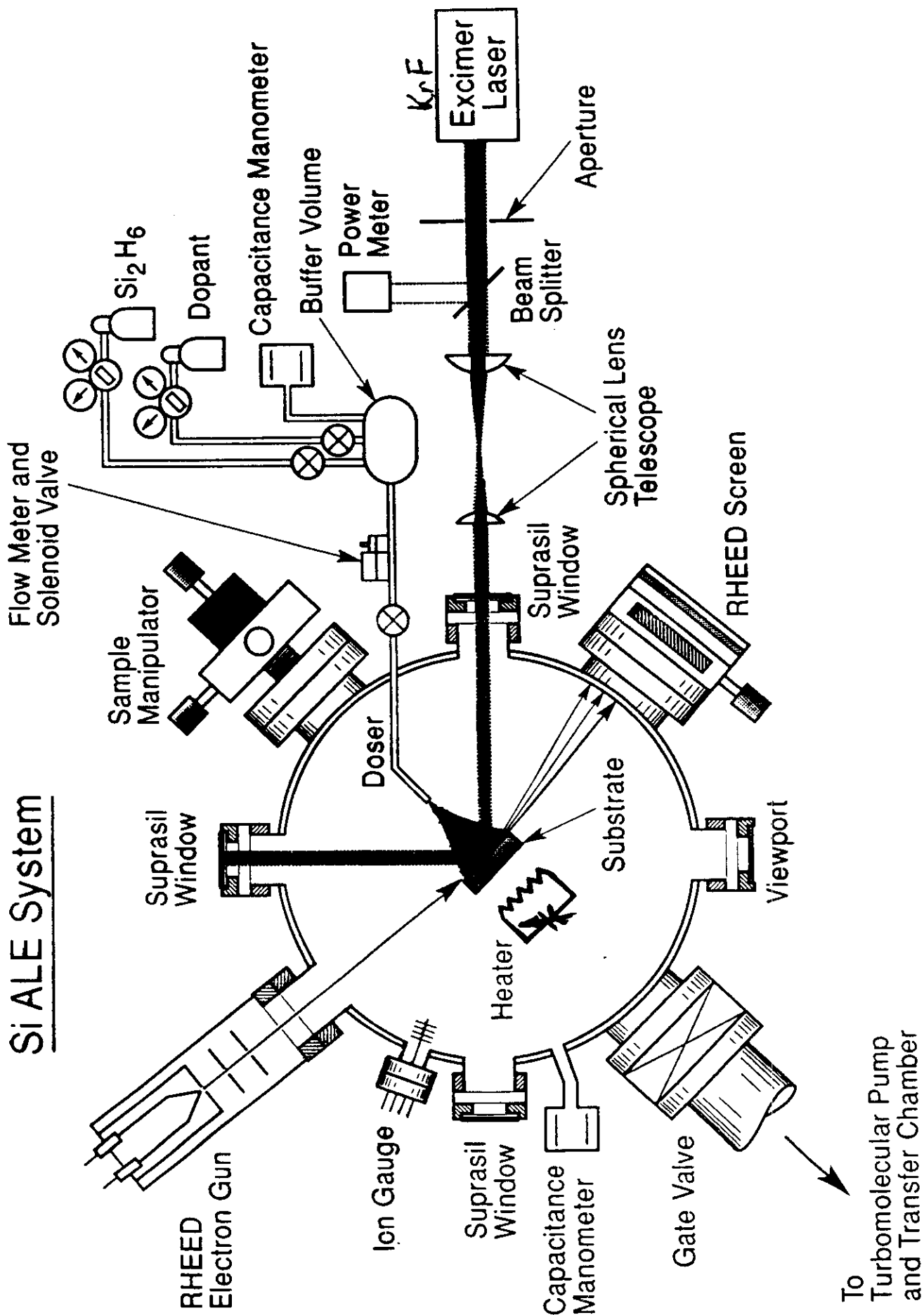
Figure 4. EELS spectra, obtained using a primary electron energy E_p of 100 eV, from a Si_2H_6 -saturated Si(100) $(1 \times 1)::2H$ dihydride surface following a 15 s anneal at (a) 300 K, (b) 655 K, (c) 705 K, (d) 765 K, (e) 845 K, and (f) 955 K.

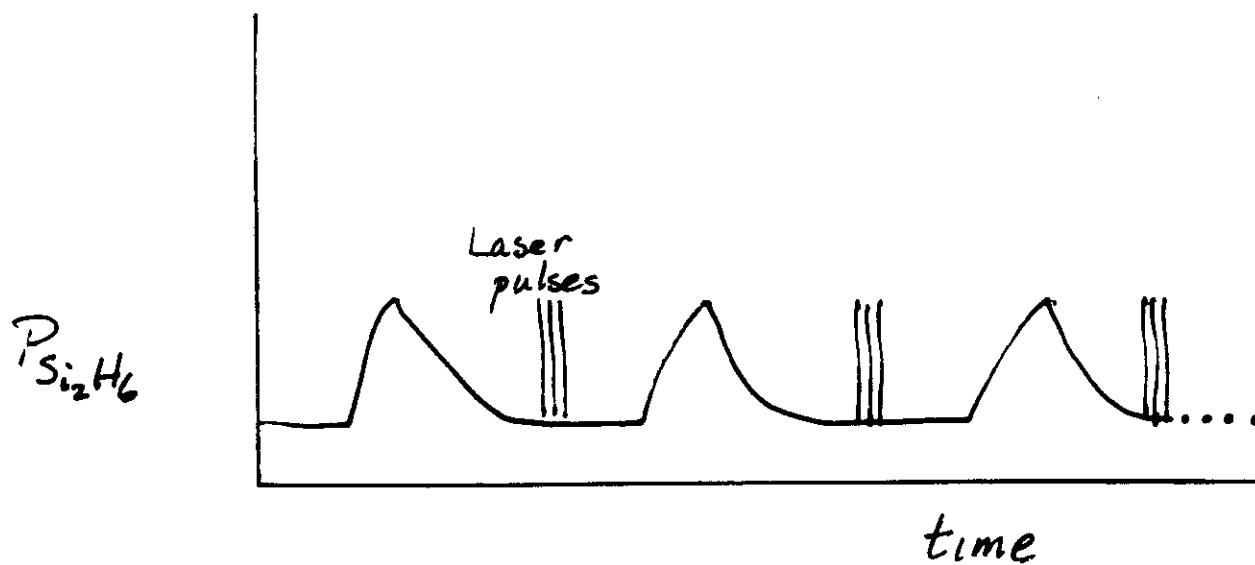
Si_2H_6 dose = $3.2 \times 10^{14} \text{ cm}^{-2}$
 $T_s = 330^\circ\text{C}$
 $200 \text{ \AA} \times 200 \text{ \AA}$



Lin, Hirschorn, Chuang, Tzu, Lubben, Greene
Phys. Rev. B

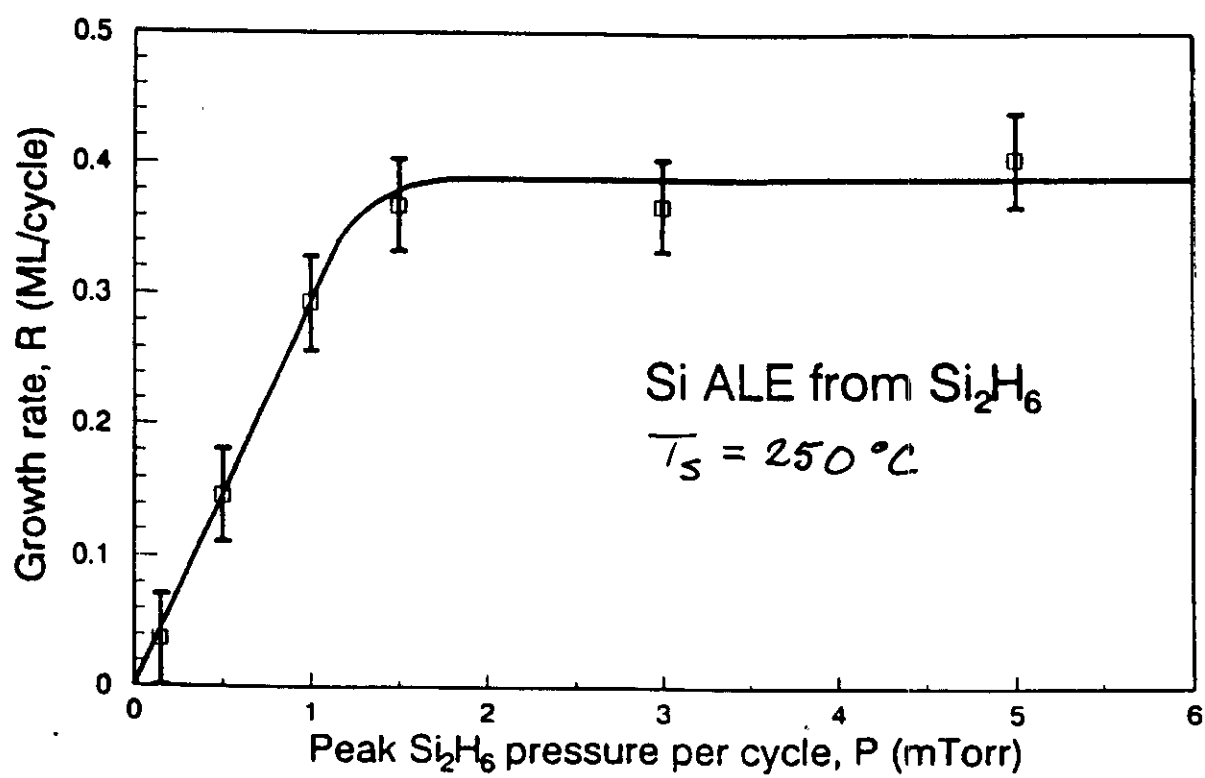
Si ALE System

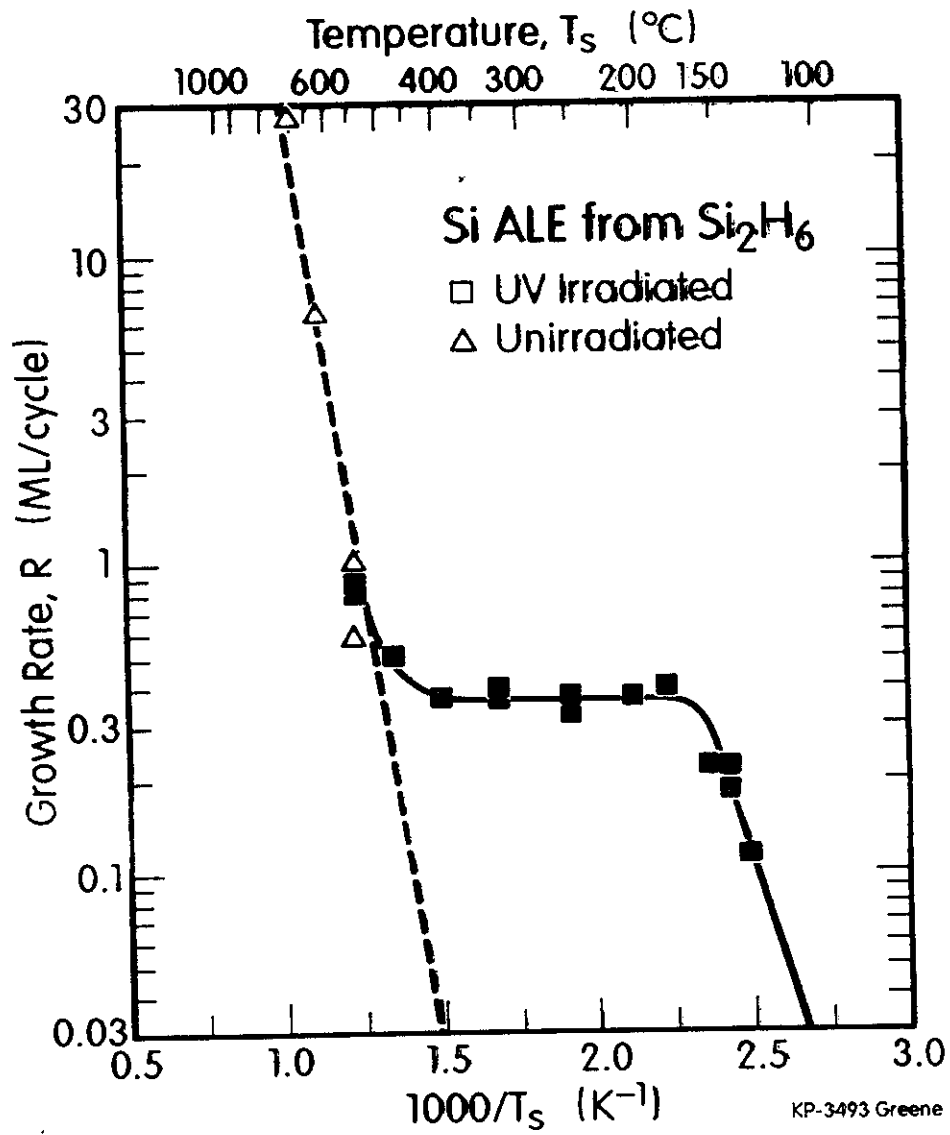




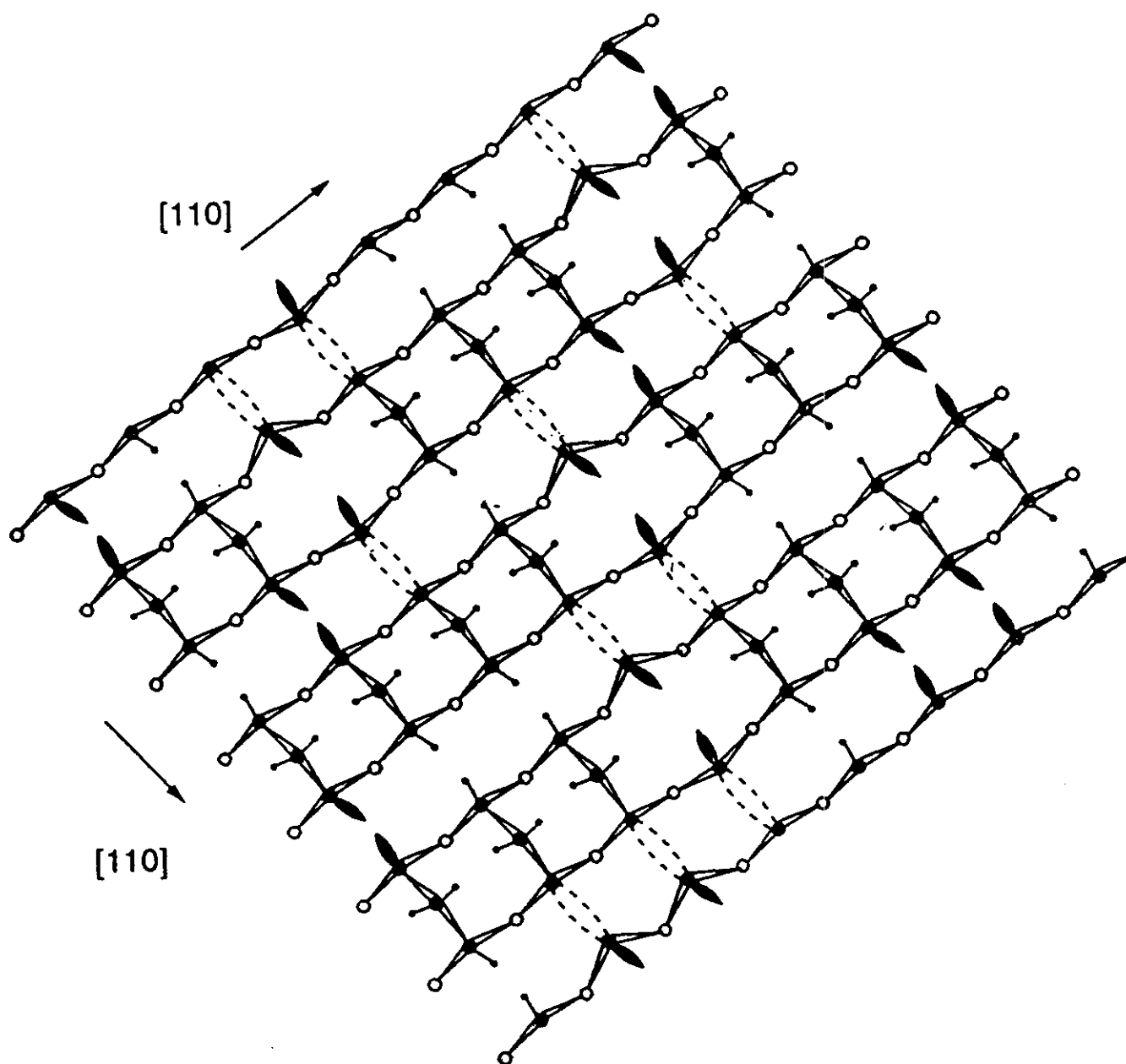
$$180^{\circ}\text{C} \leq T_s \leq 400^{\circ}\text{C}$$

$$P_{\text{max}} \geq 1.5 \text{ mTorr}$$



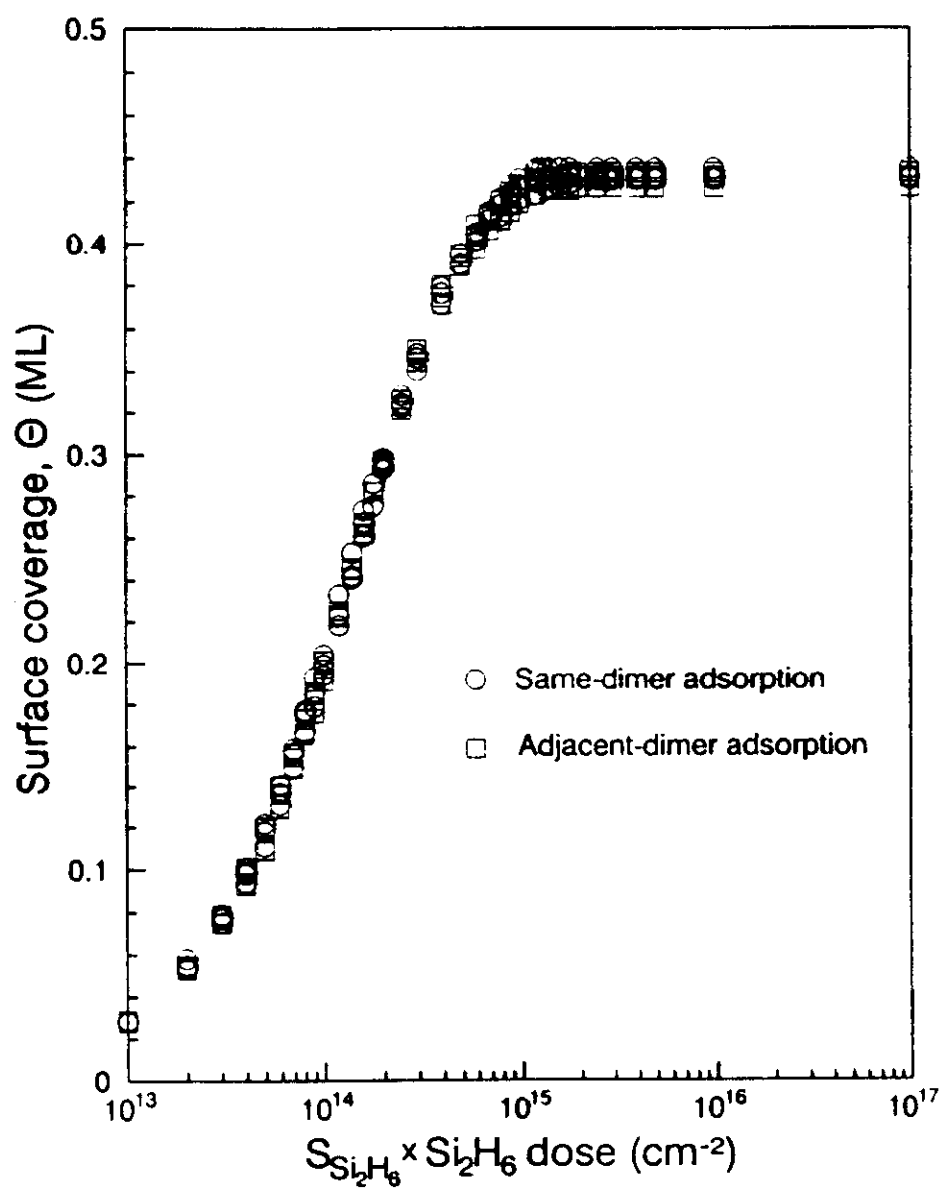


Lubben, Tsu, Bramblett, Greene, JVST A



- = Surface Si atom
- = Adsorbed Si atom
- = H atom
- ◐ = Dangling bond
- ≡ = Si-Si bond

D.S. Liñ, T.-C. Chuang, R. Tsu, J.E. Greene,
 Phys. Rev. B, *in press.*



Analytical Transition-State Model

Si(001) 2x1 ALE

$$\frac{dn_{\text{SiH}_3}}{dt} = 2 J_{\text{Si}_2\text{H}_6} S_{\text{Si}_2\text{H}_6}(T_s) [1 - N_{\text{oc}} - N_{\text{bl}}] - n_{\text{SiH}_3} k_{\text{d}, \text{SiH}_3} - (n_{\text{SiH}_3})^2 k_{\text{a}, \text{Si}_2\text{H}_6} - \underline{n_{\text{SiH}_3} k_{\text{dis}, \text{SiH}_3}}$$

$$\frac{dn_{\text{SiH}_2}}{dt} = \underline{n_{\text{SiH}_3} k_{\text{dis}, \text{SiH}_3}} - n_{\text{SiH}_2} k_{\text{d}, \text{SiH}_2} - n_{\text{SiH}_2} k_{\text{dis}, \text{SiH}_2}$$

$$\underline{k_{\text{dis}, \text{SiH}_3}} = \nu e^{(-E_{\text{dis}, \text{SiH}_3}/kT_s)}$$

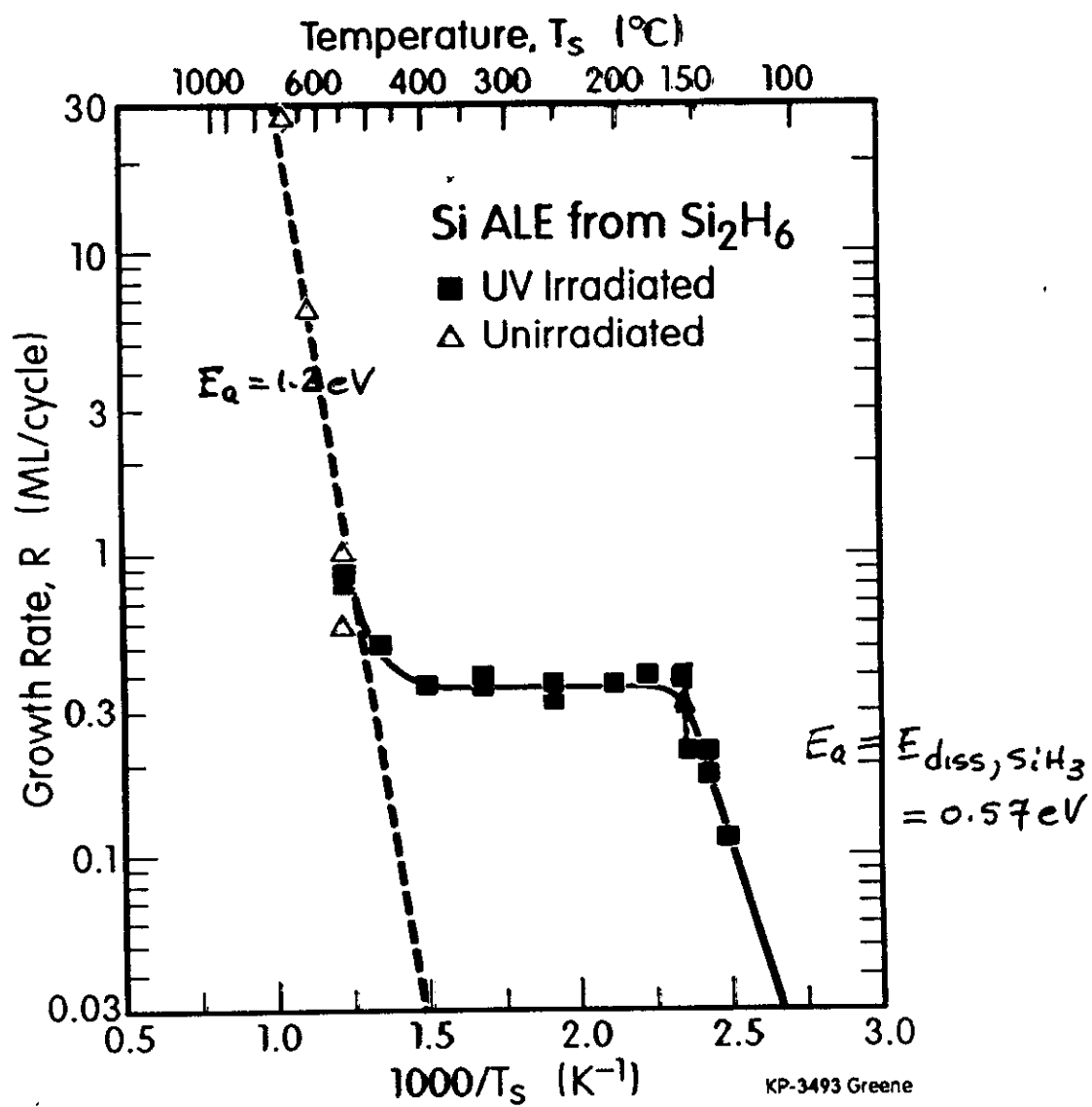
$$N_{\text{un}} + N_{\text{oc}} + N_{\text{bl}} = 1$$

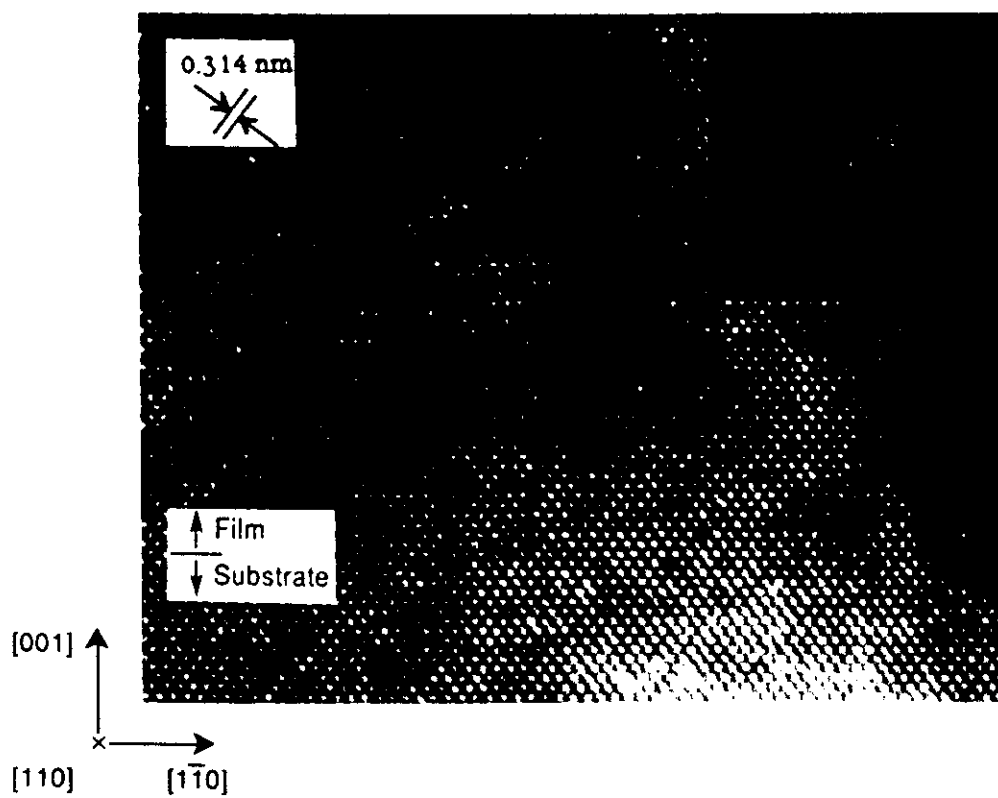
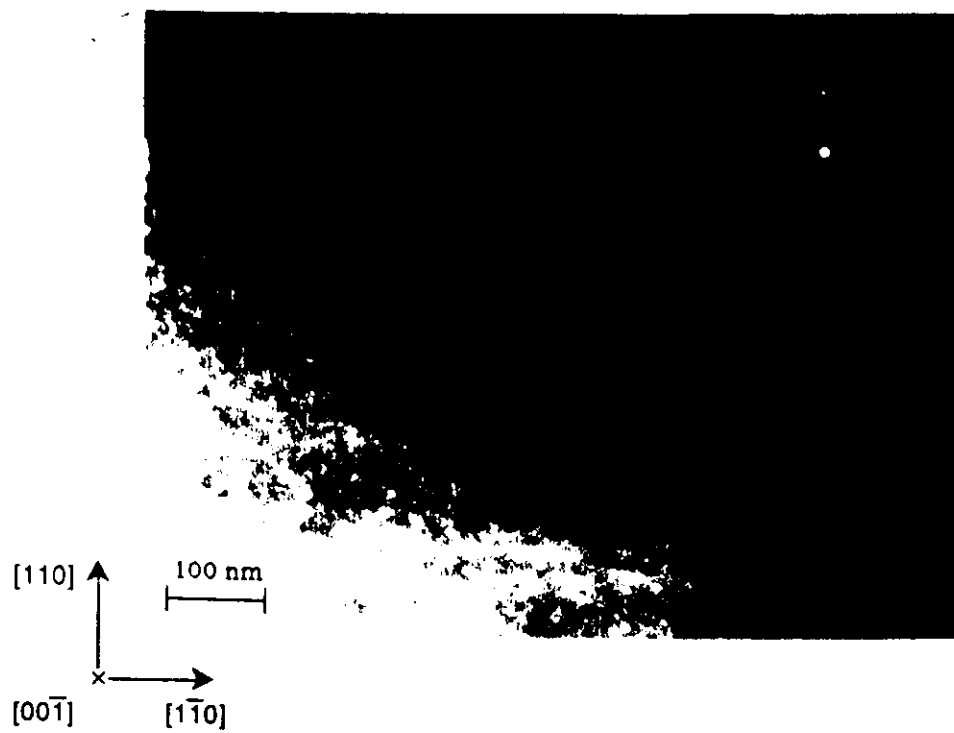
Monte Carlo simulation $\rightarrow N_{\text{bl}} = f(N_{\text{oc}})$

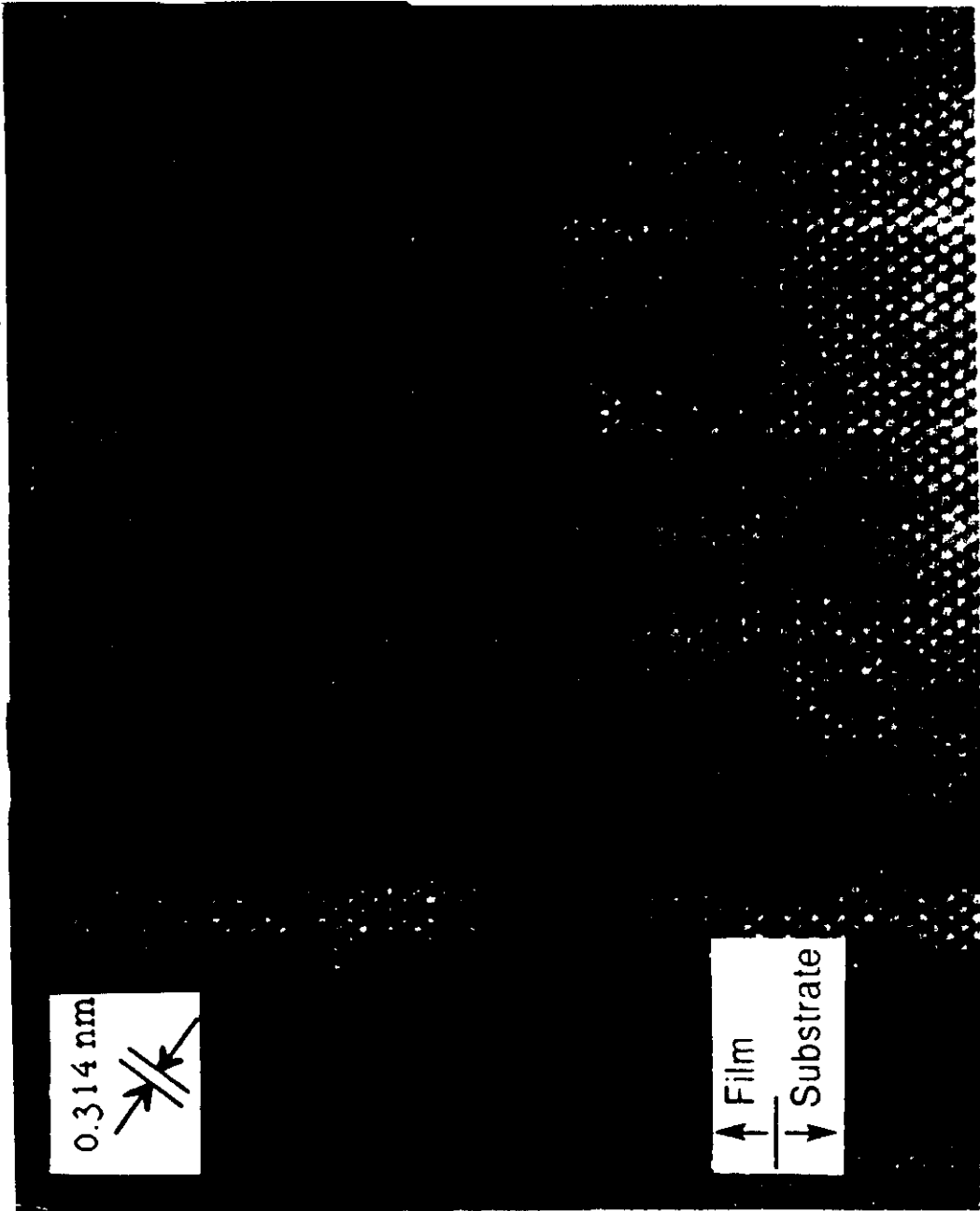
$$n_{\text{SiH}_3}^* \approx 0.4 n_s - n_{\text{SiH}_2}^*$$

$$\boxed{n_{\text{SiH}_2}^* = 0.4 n_s \Delta t \nu e^{(-E_{\text{dis}, \text{SiH}_3}/kT_s)}}$$

$$\therefore \text{ALE: } R = n_{\text{Si}}^* = n_{\text{SiH}_2}^* \approx 0.4 \text{ ML/cycle}$$





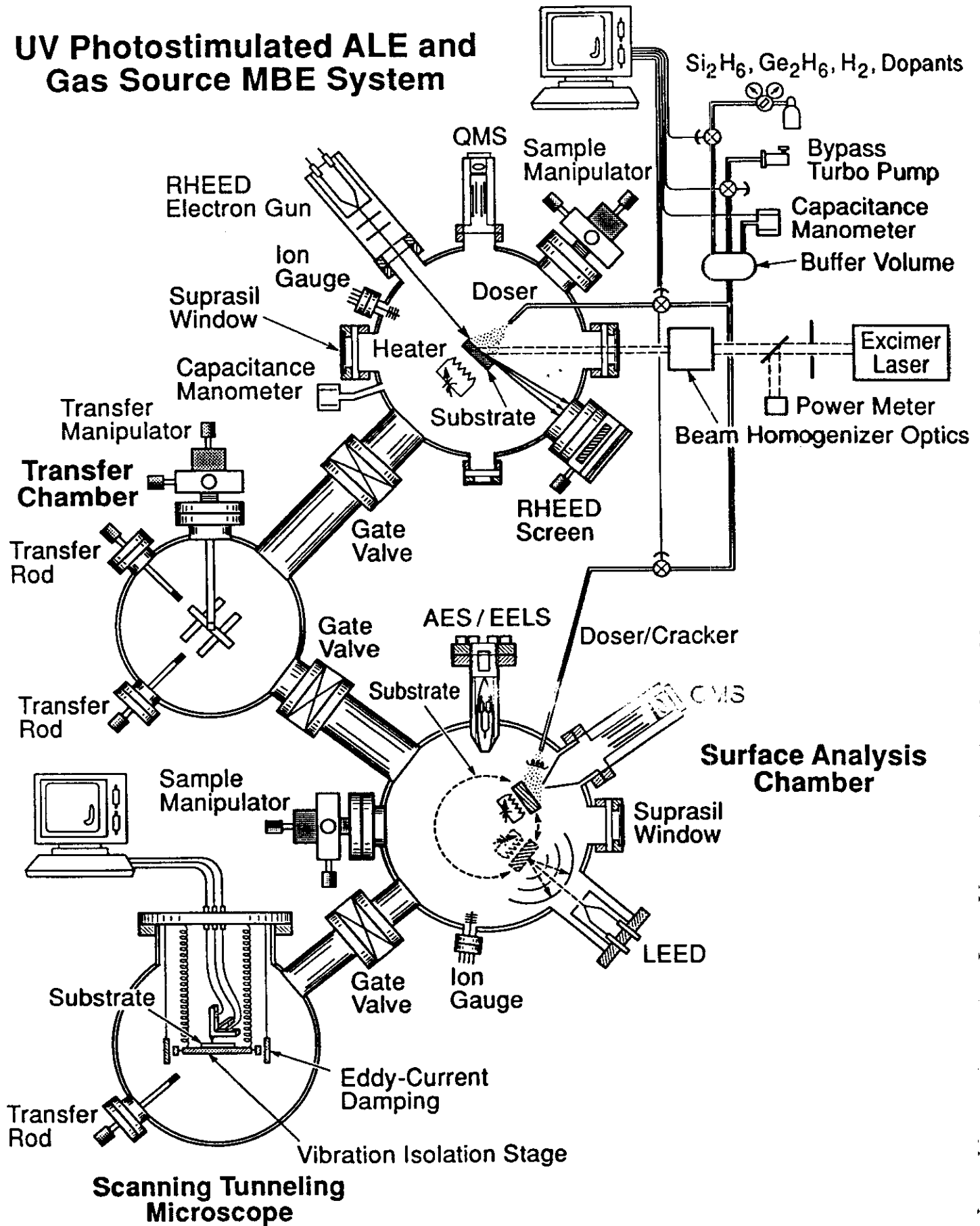


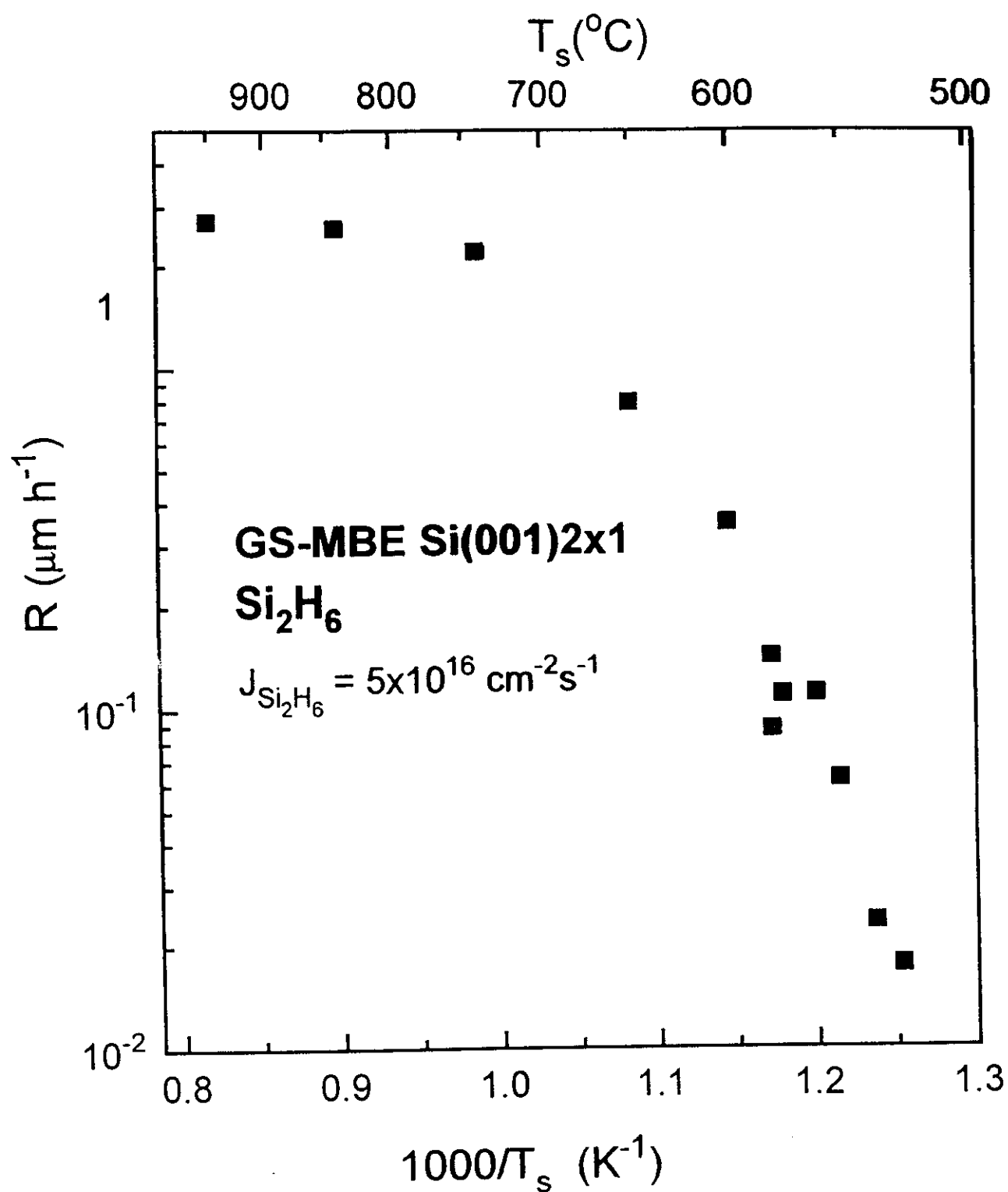
0.314 nm

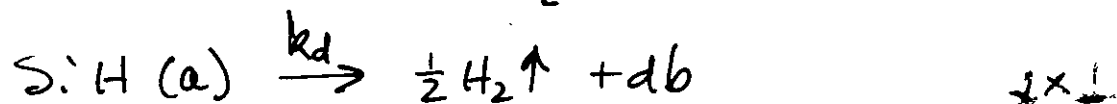
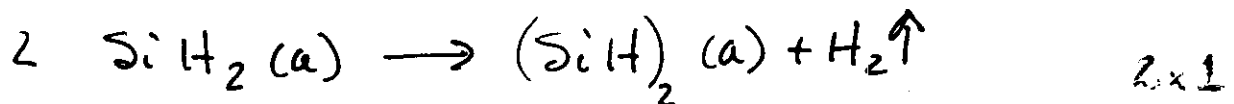
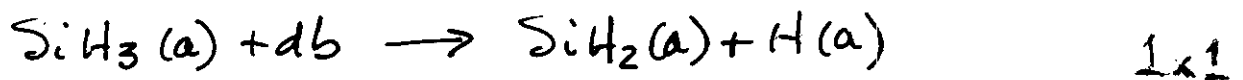
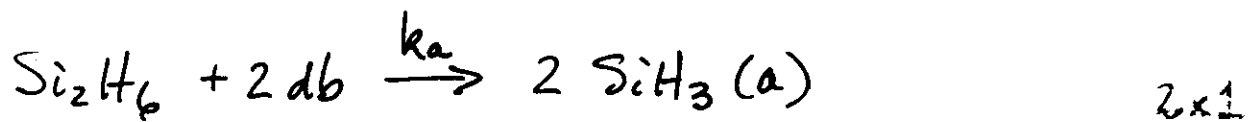
↑ Film
↓ Substrate

[001] [110] [$\bar{1}\bar{1}0$]

UV Photostimulated ALE and Gas Source MBE System







$$\frac{d\theta_{\text{db}}}{dt} = -2k_a J_{\text{Si}_2\text{H}_6} \theta_{\text{db}}^2 + k_d (1 - \theta_{\text{db}})$$

∴ at steady state:

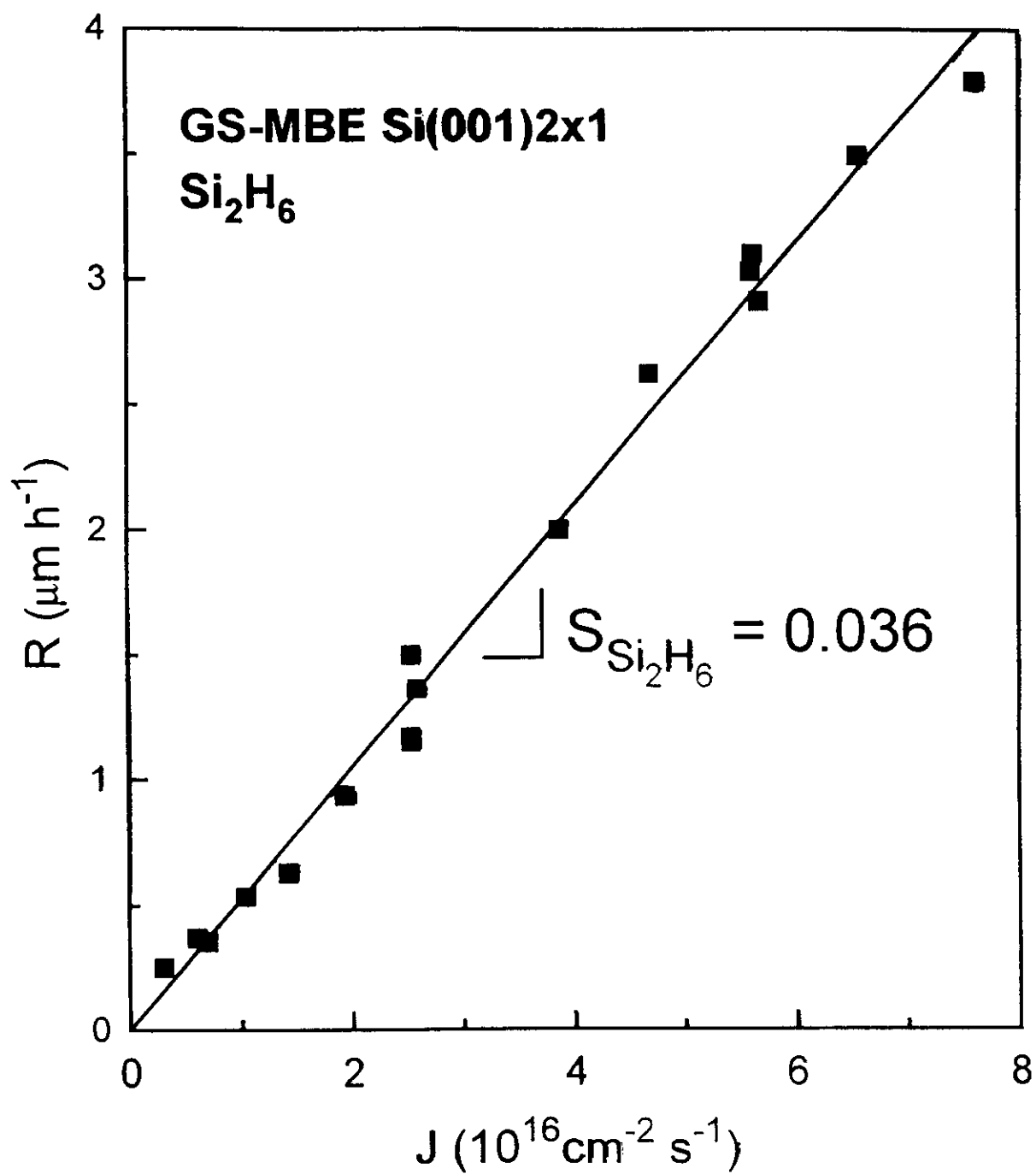
$$\theta_{\text{db}} = \frac{k_d}{4k_a J_{\text{Si}_2\text{H}_6}} \left[\left(1 + \frac{8k_a J_{\text{Si}_2\text{H}_6}}{k_d} \right)^{1/2} - 1 \right]$$

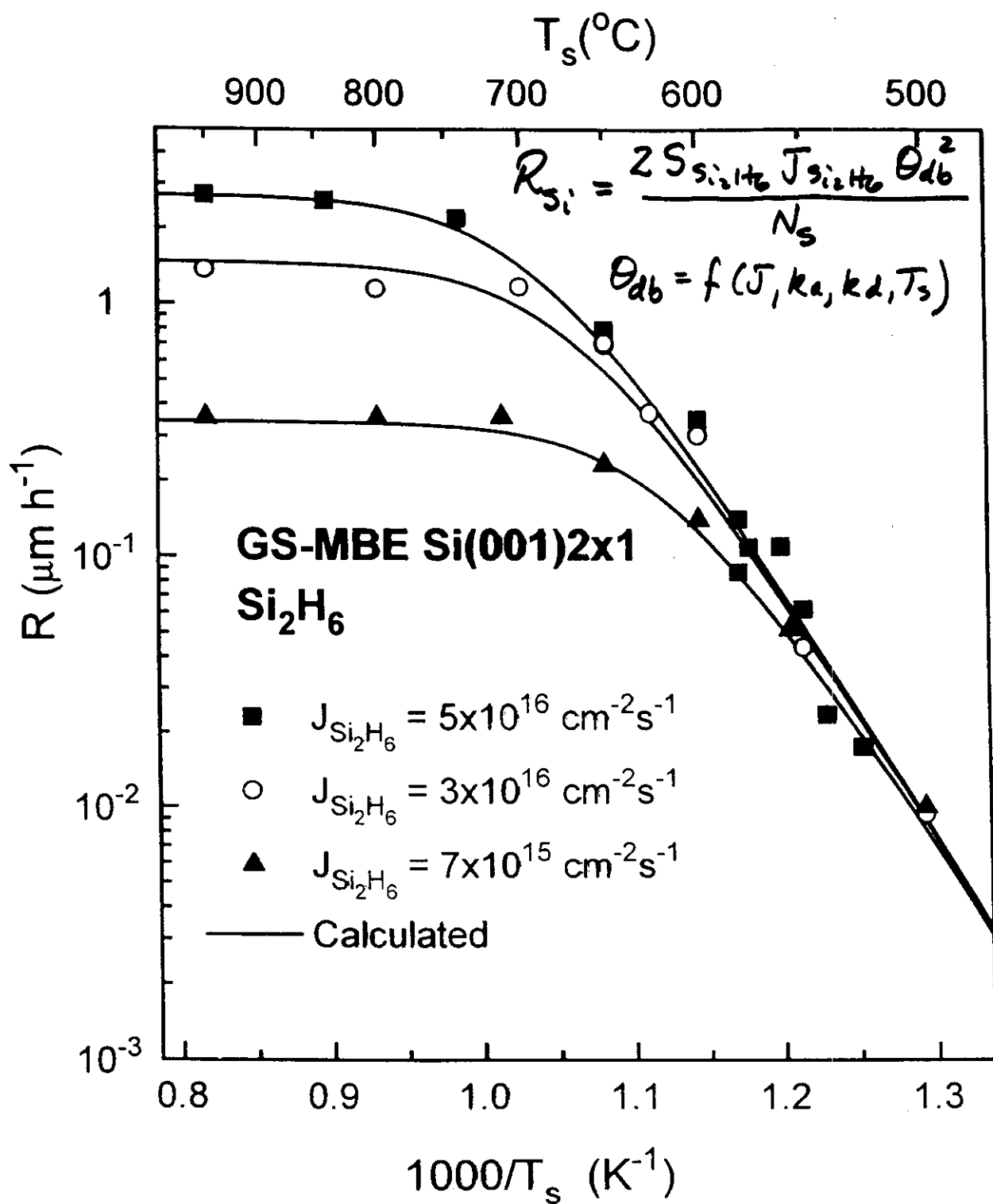
$$R = \frac{2N_s k_a J_{\text{Si}_2\text{H}_6} \theta_{\text{db}}^2}{N}$$

where $k_a = S_{\text{Si}_2\text{H}_6} / N_s$ (measured)

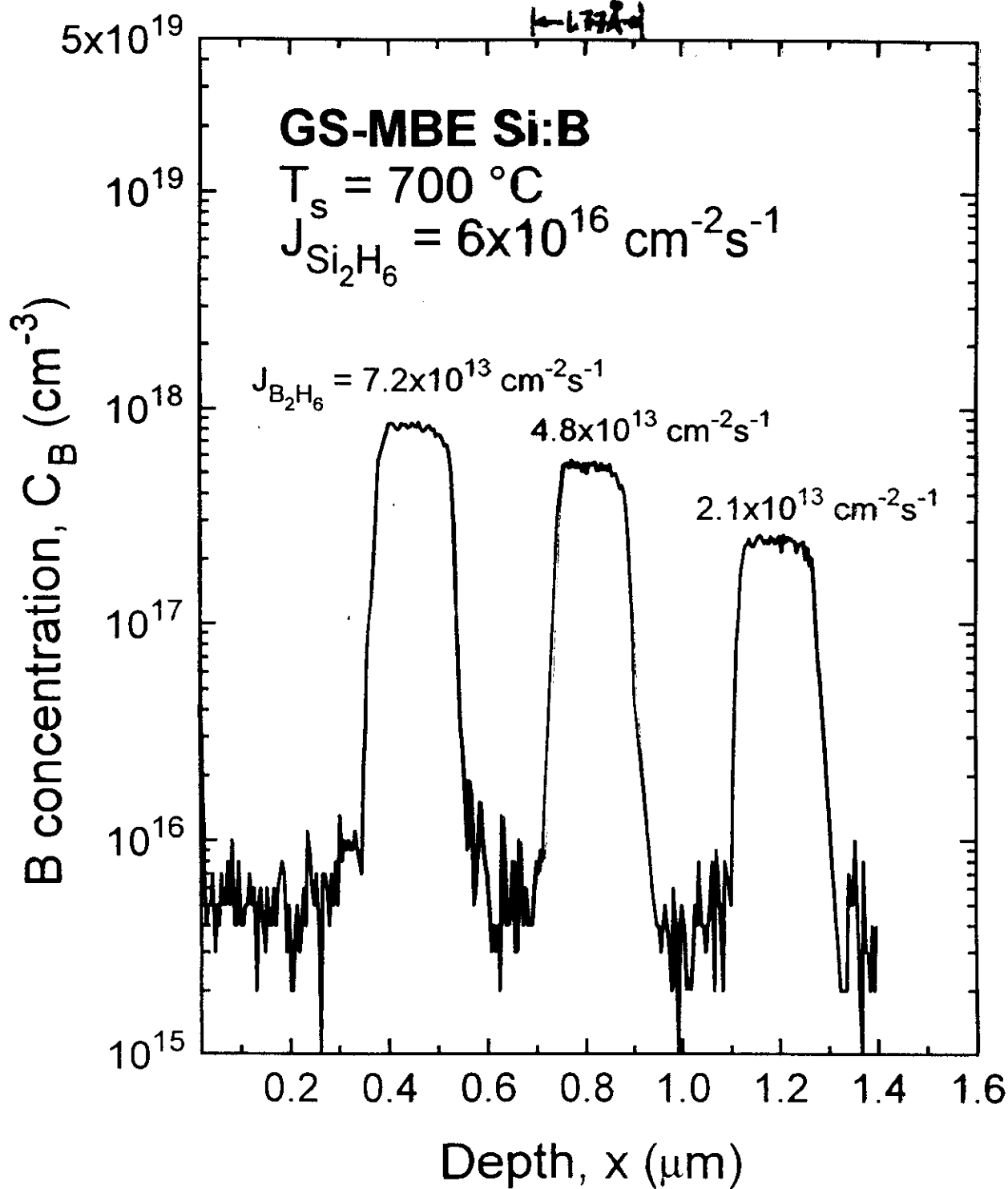
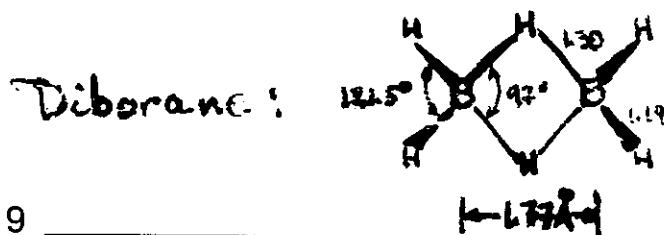
$$k_d = 7.9 \times 10^{11} \exp\left(\frac{2.04\text{eV}}{kT_s}\right) \text{ s}^{-1}$$

(Yates et. al., JCP
92, 5700 (1990)).

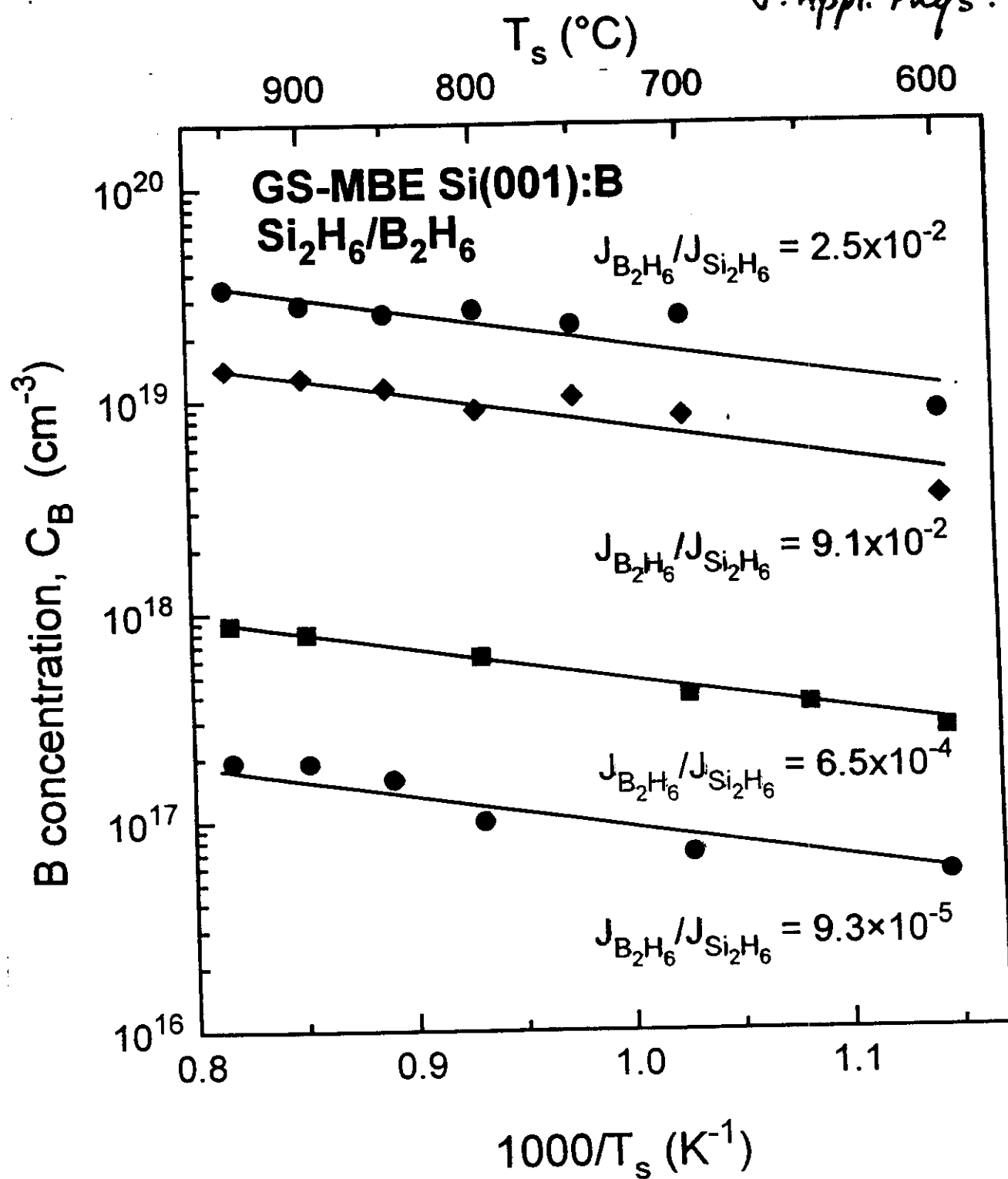




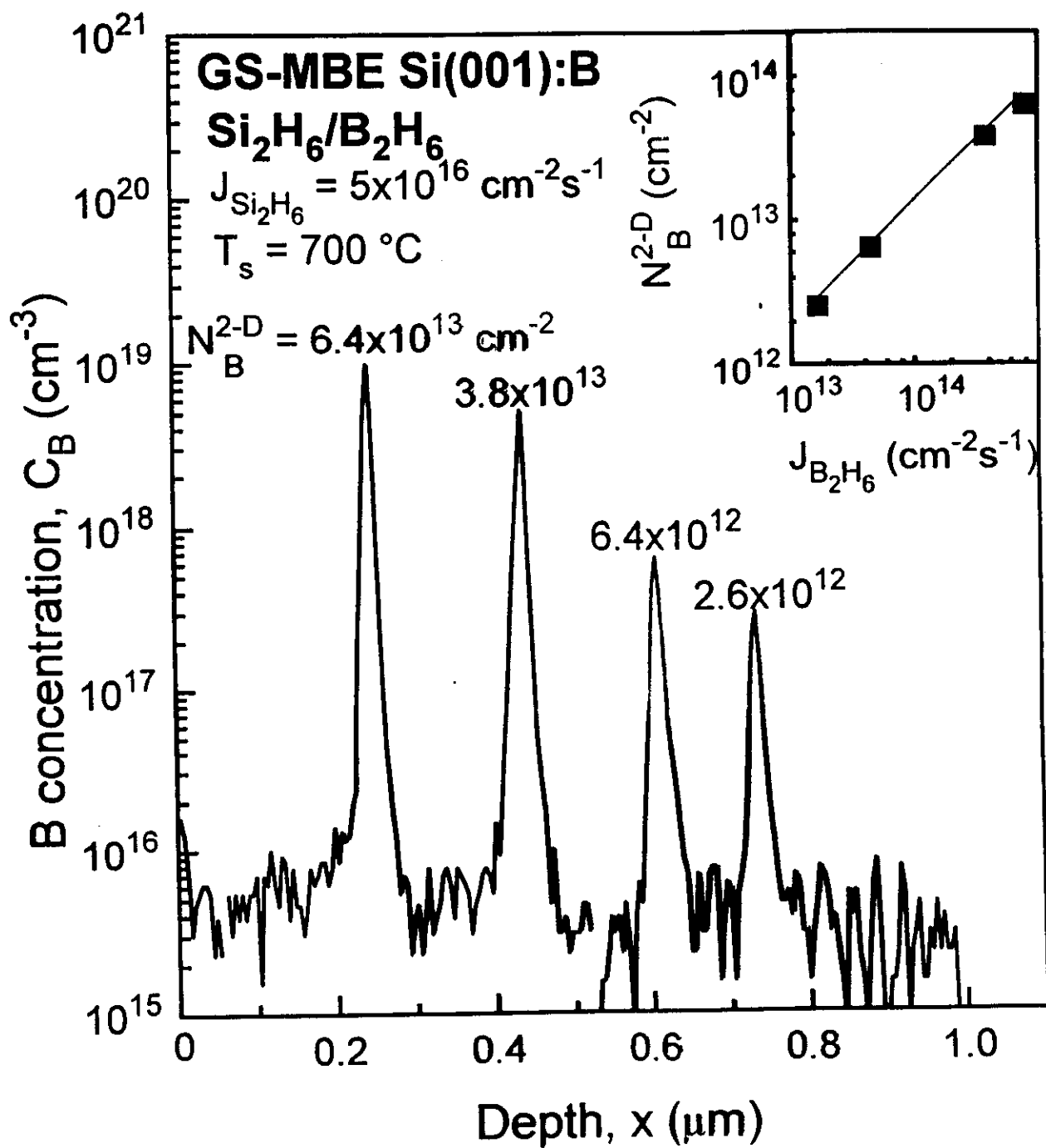
T.R. Bramblett, Q. Lu, T. Karazawa, M.A. Hasan,
S.K. Jo, and J.E. Greene, J. Appl. Phys.

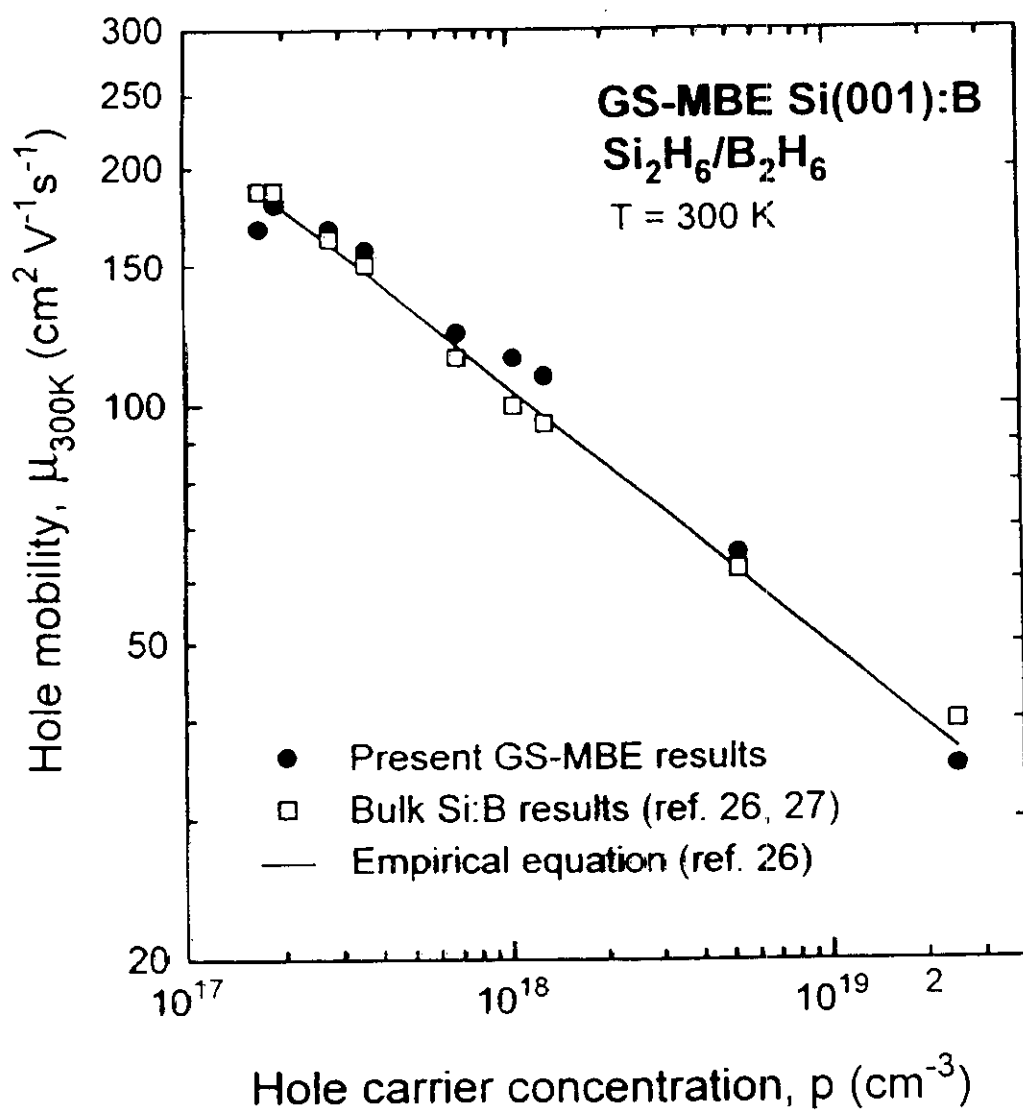


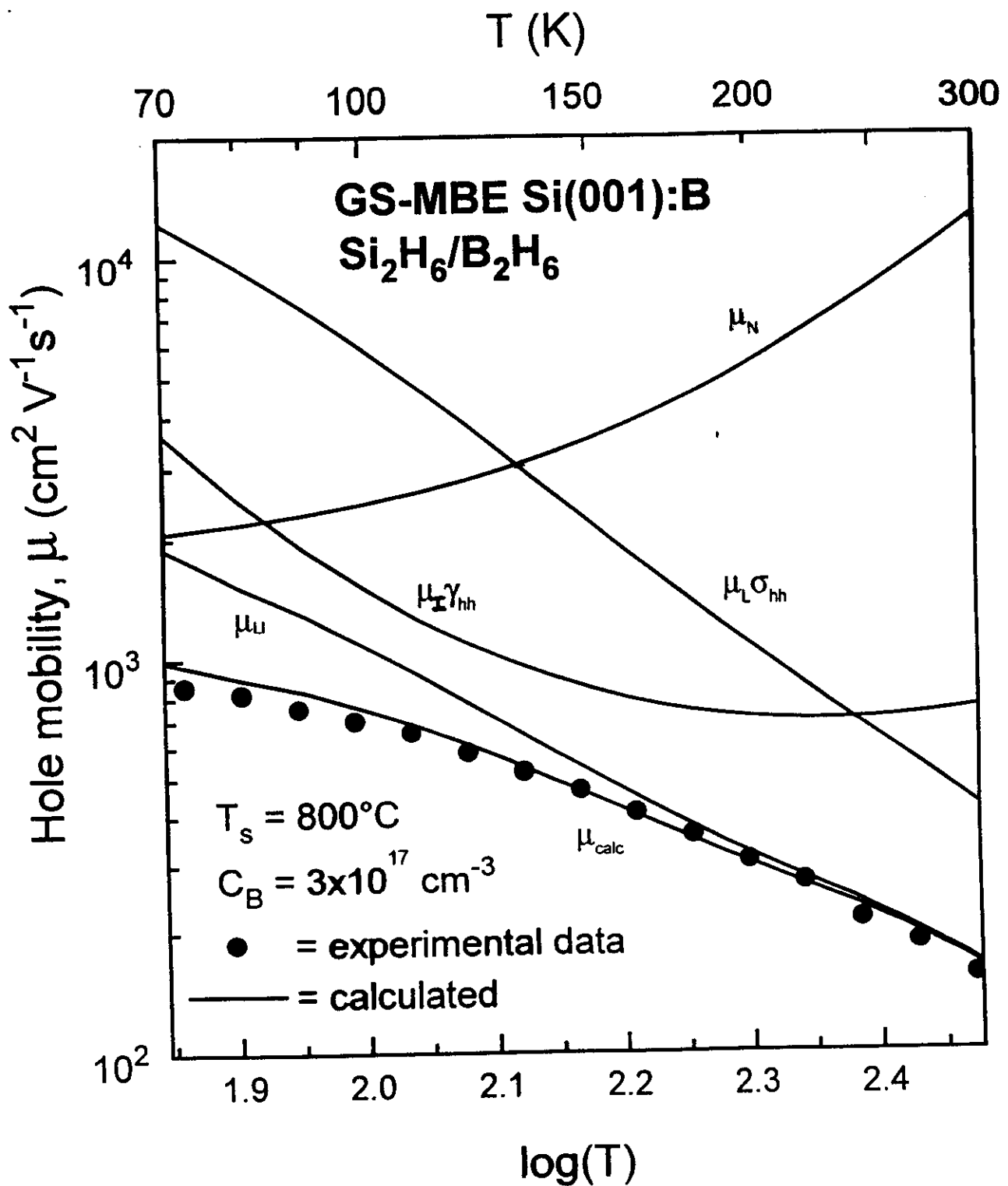
Lu, Bramblett, Lee, Hasan, Kawasaki, Greene
J. Appl. Phys.



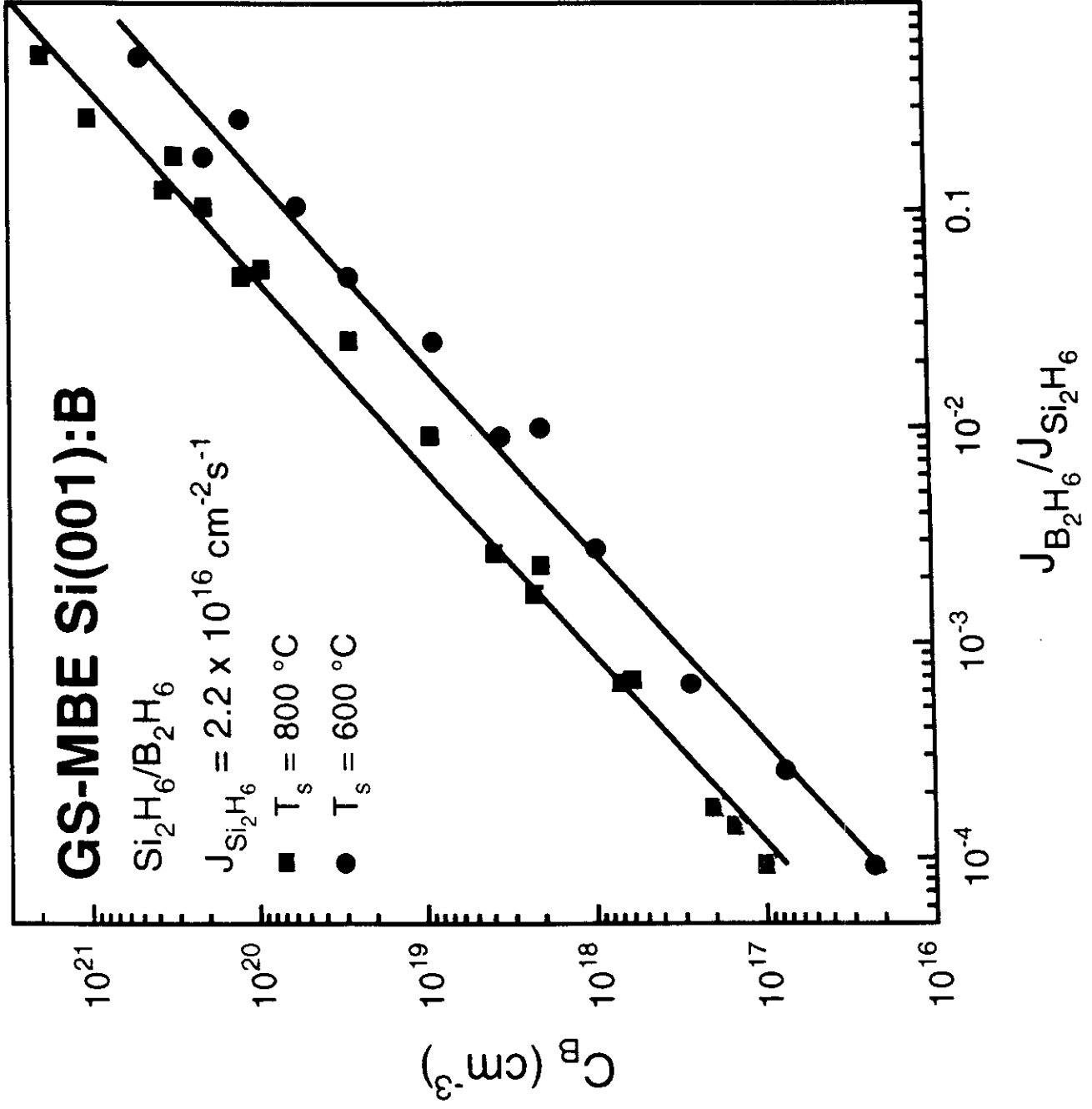
$$S_{B_2H_6/Si(001)} = \frac{6.4 \times 10^{-4}}{1.4 \times 10^{-3}} \quad @ \quad \begin{matrix} 600^\circ C \\ 950^\circ C \end{matrix}$$





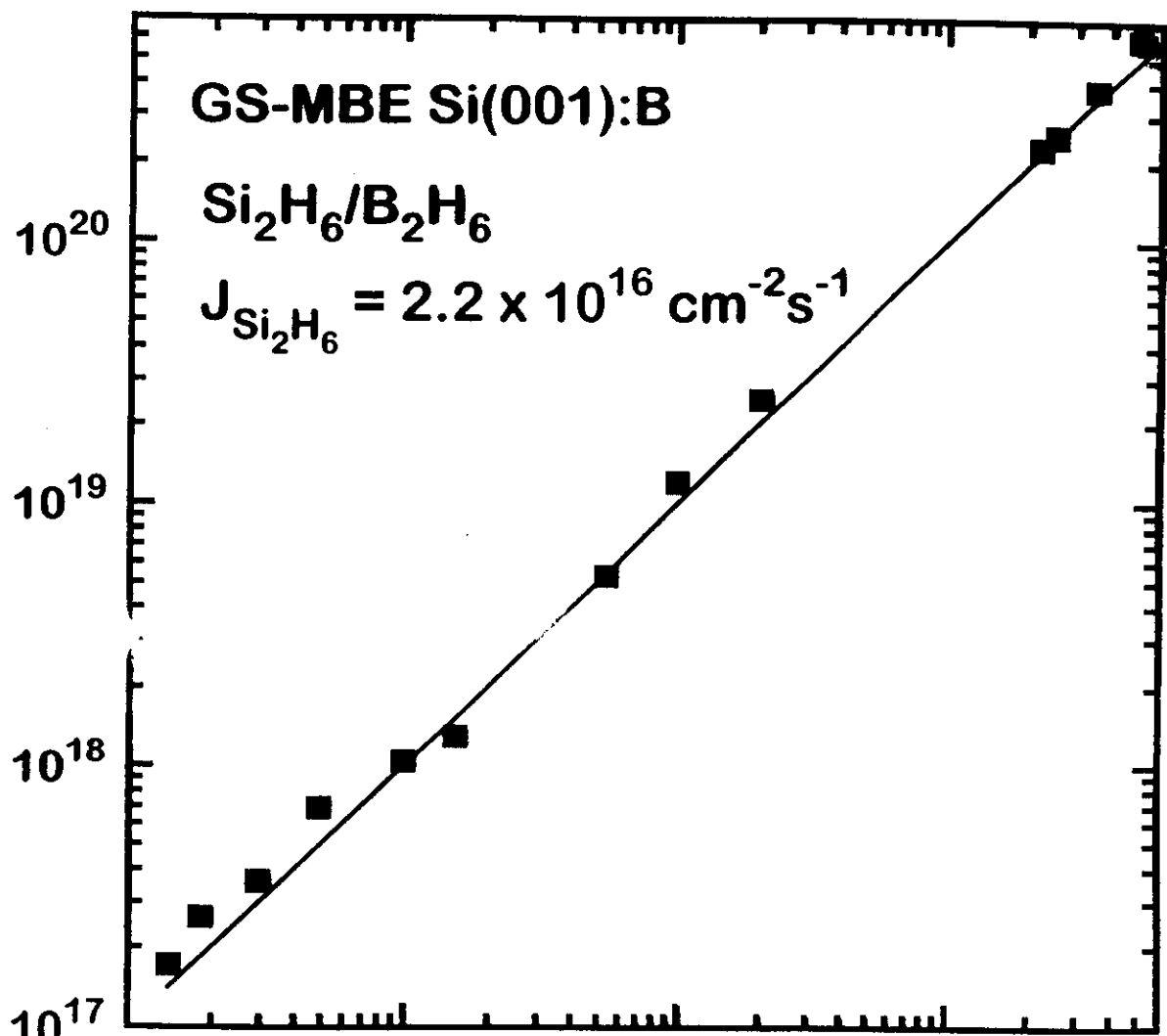


Lu, Bramblett, Lee, Hasan, Karasawa, Greene
J. Appl. Phys. 77, 3067 (1995)



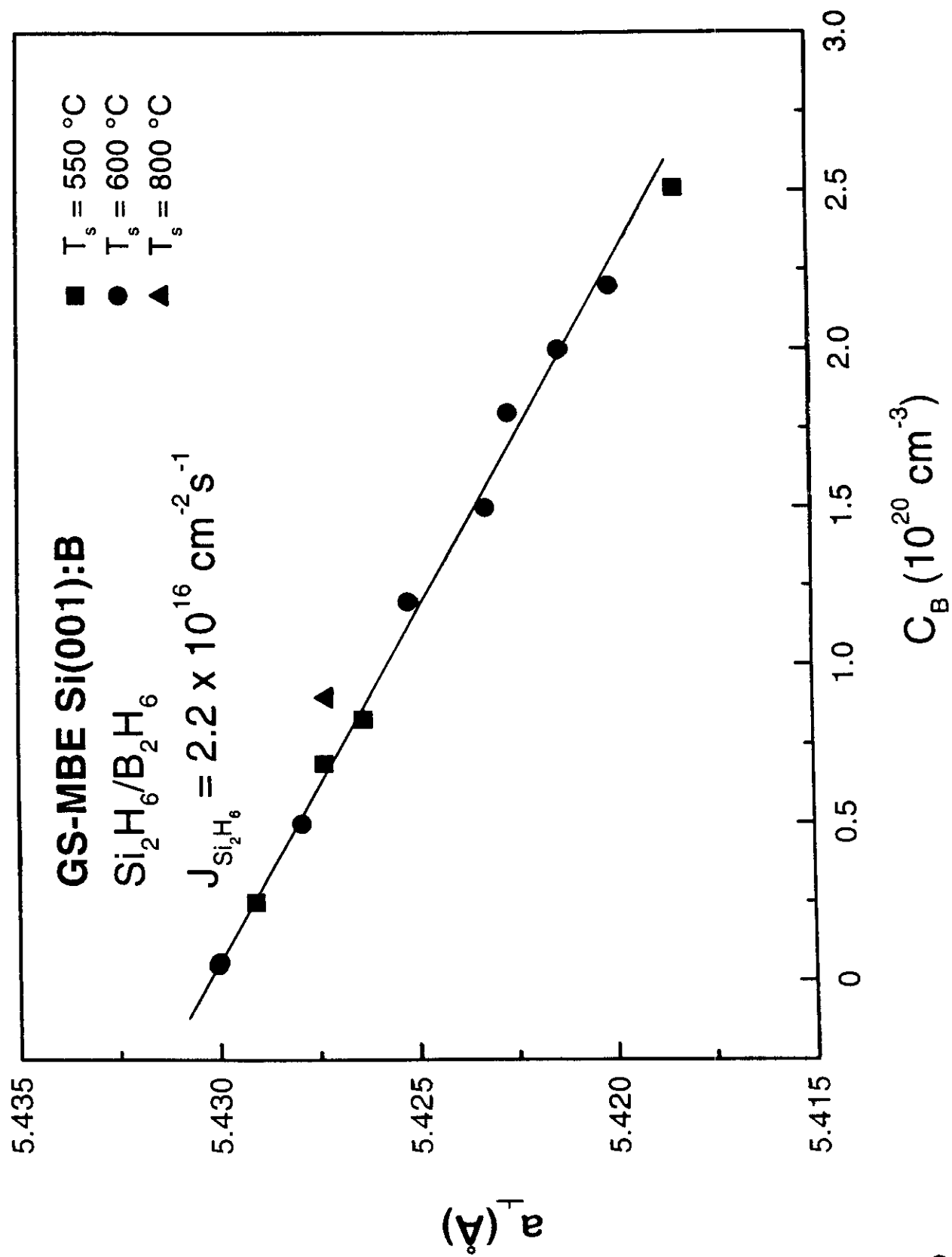
*B acceptor concn.
(Hall meas.)*

N_B (cm⁻³)



C_B (cm⁻³)

*Total B concn
(SIMS meas.)*

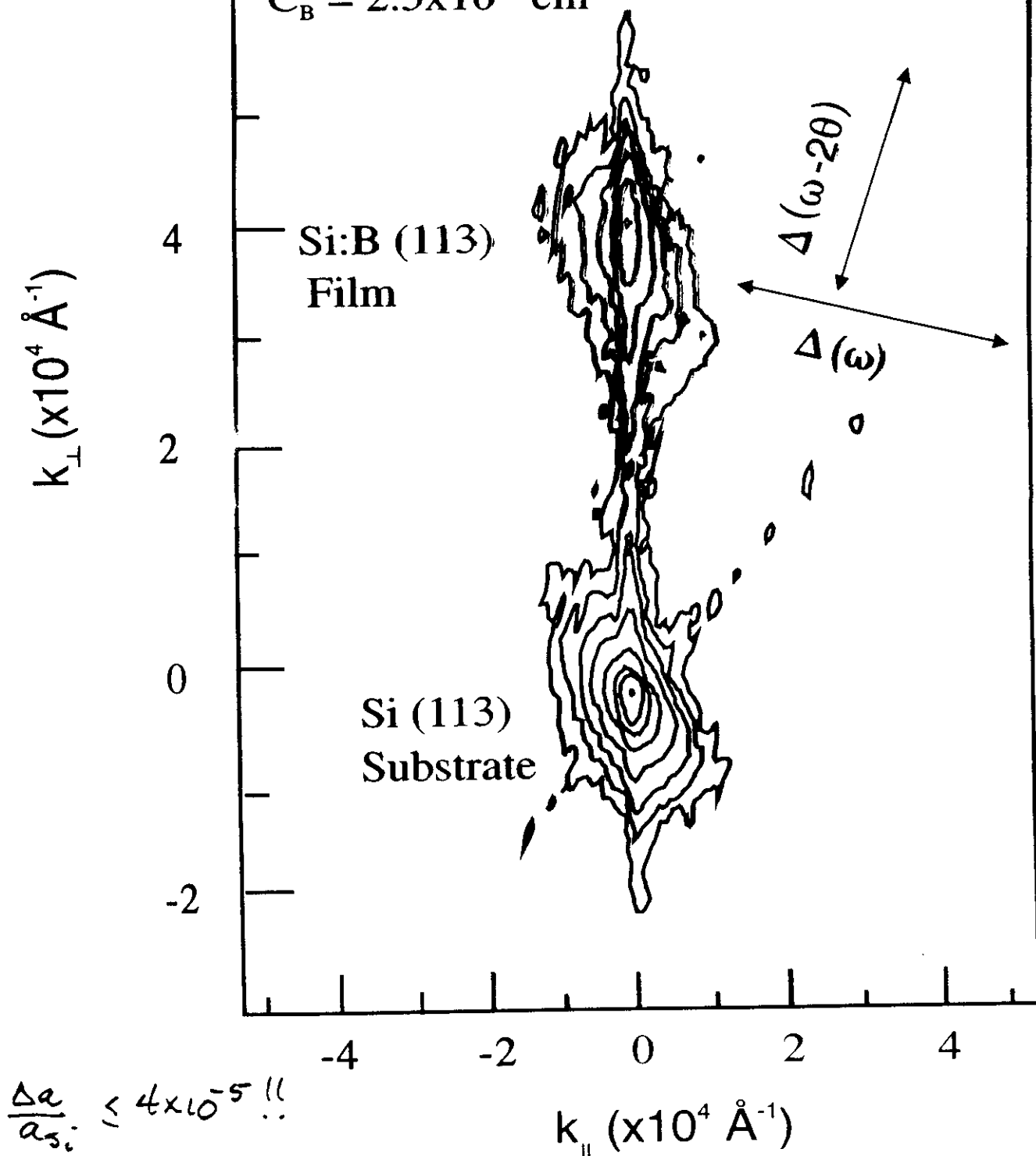


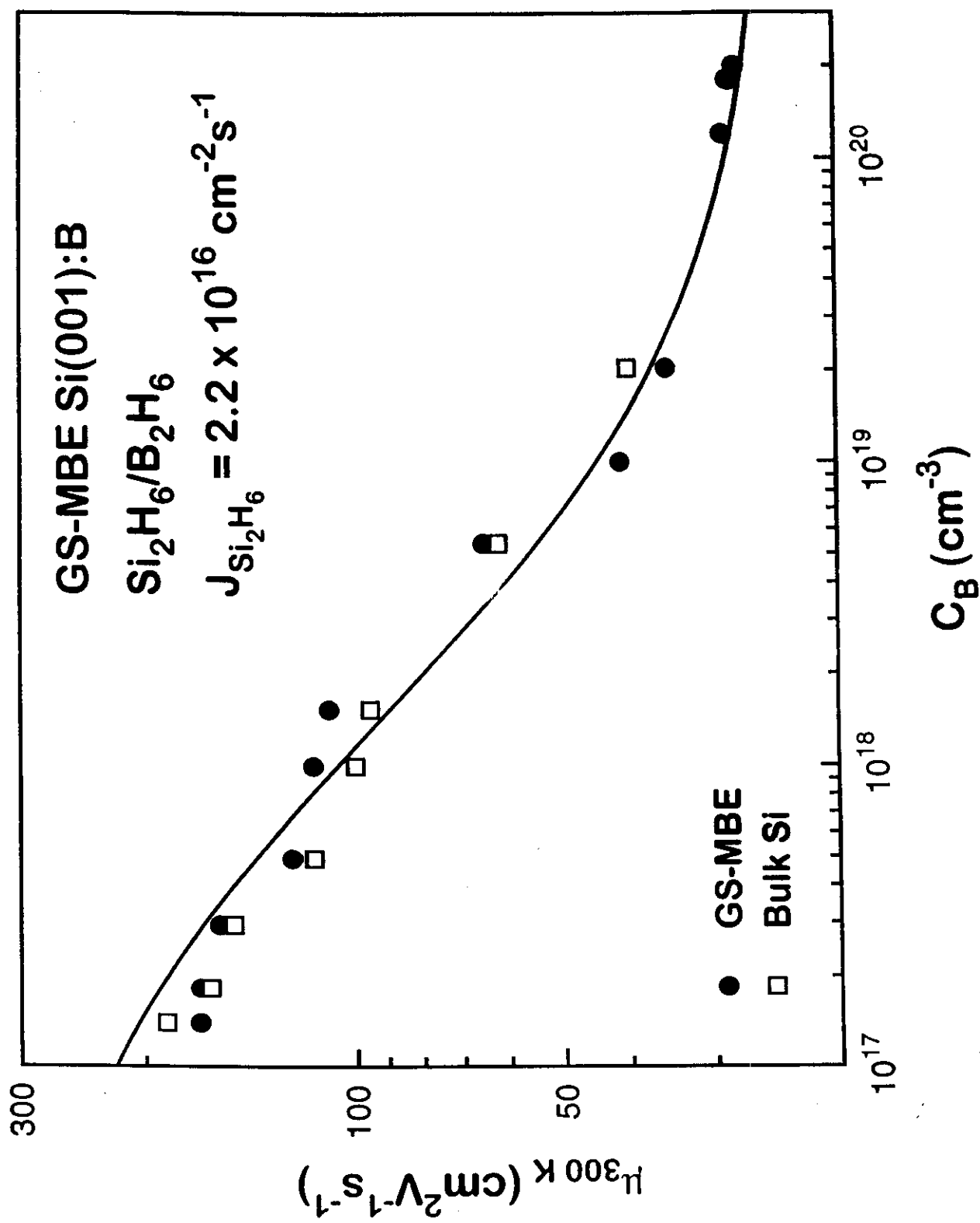
GS-MBE Si(001):B

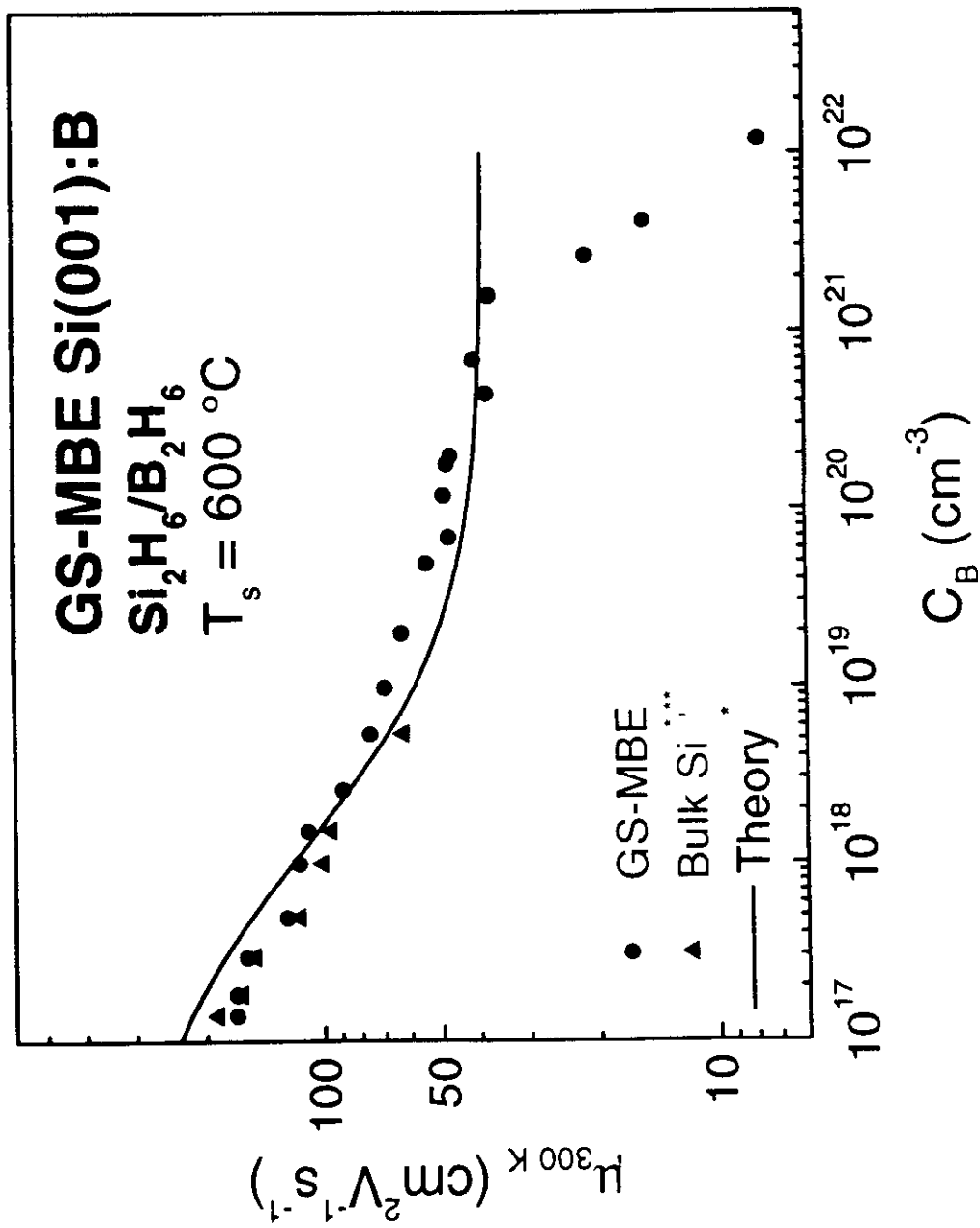
$\text{Si}_2\text{H}_6/\text{B}_2\text{H}_6$

$T_s = 600^\circ \text{C}$

$C_B = 2.5 \times 10^{20} \text{ cm}^{-3}$

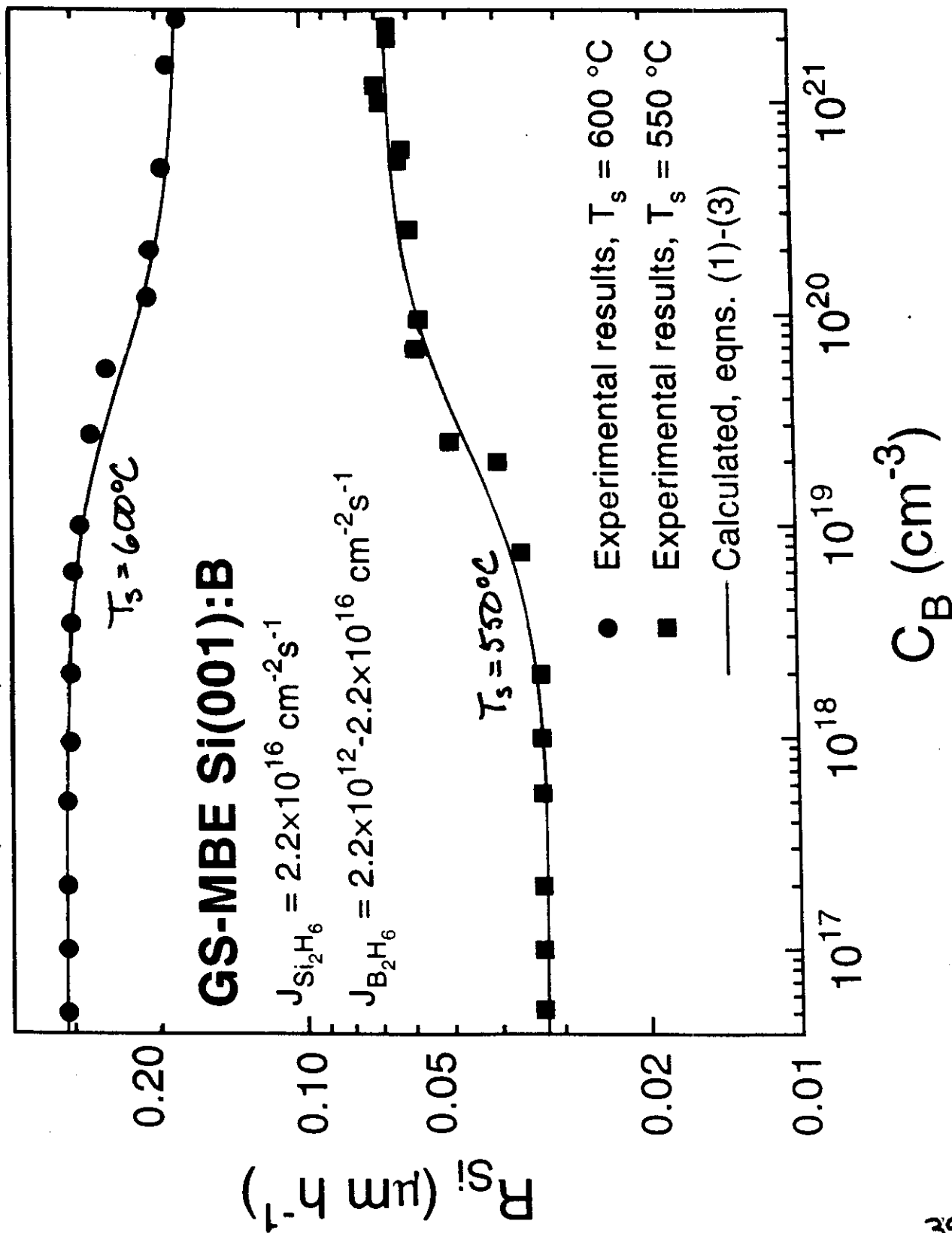


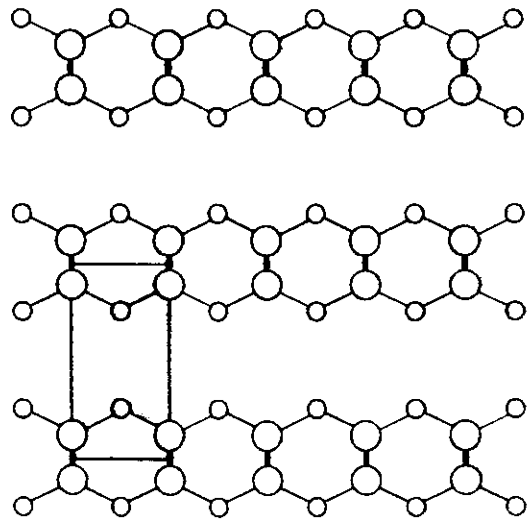




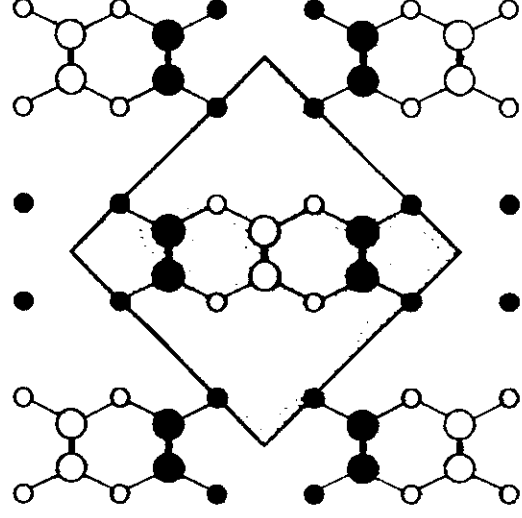
*D. Caughy, R. Thomas, Proc. IEEE 55 2192 (1967).
 G. A. Slack, and M. A. Hussain J. Appl. Phys., 70, 2694 (1991).
 **S. Wagner, J. Electrochem. Soc. 119 1570 (1972).

Glass, Kim, Sardela, Lu, Carlsson, Abelson, Greene, Surf. Sci. 392, 463 (1997).

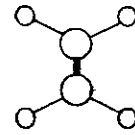




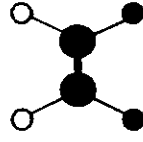
2×1 reconstruction



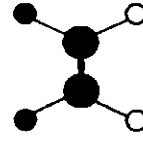
c(4×4) local structure



dimer unit

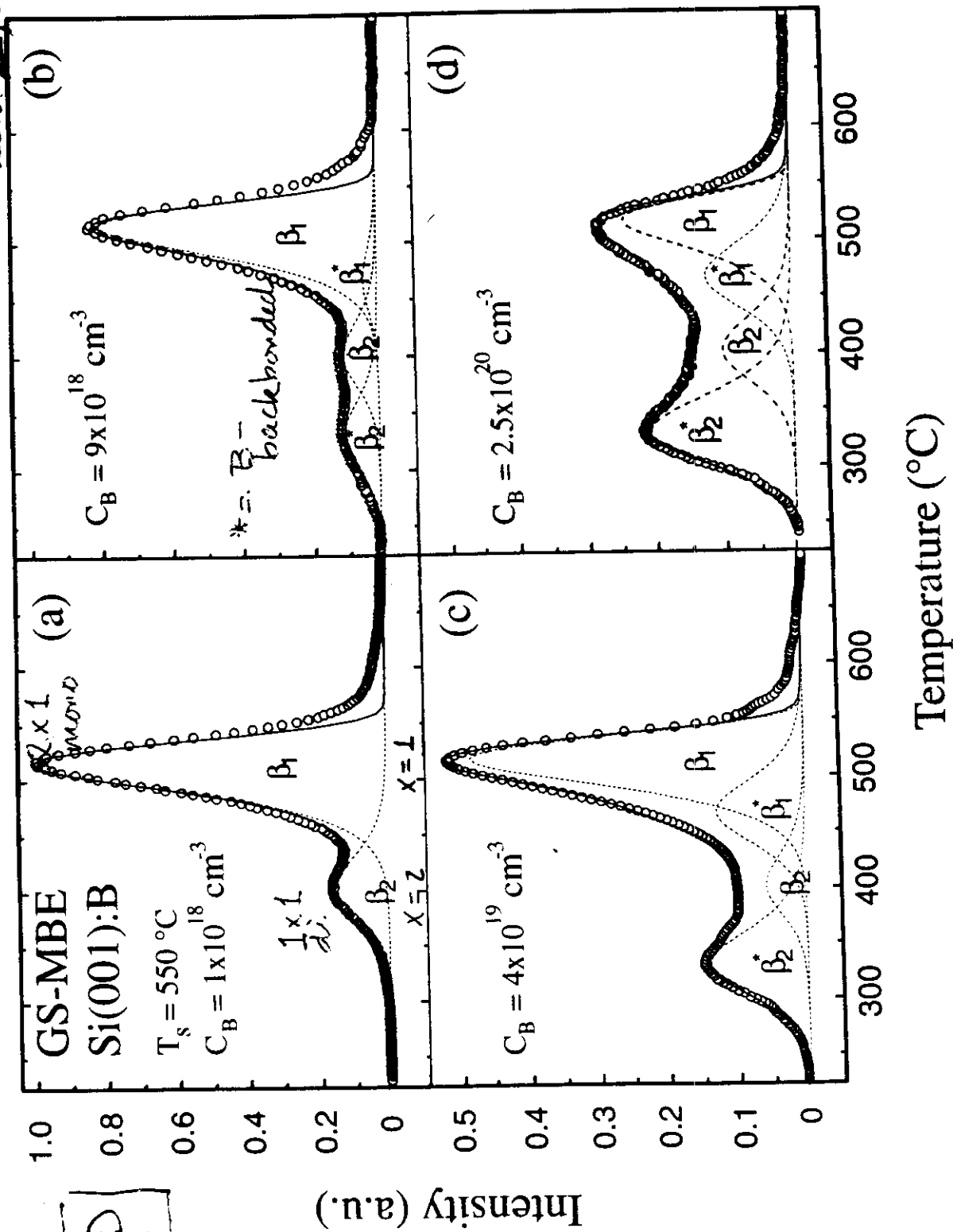


dimer unit



B-backbonded ○ ● top layer Si atoms
dimer unit ● ○ 2nd layer B atoms
 ○ 2nd layer Si atoms

Kim, Glass, Park, Spila, Taylor, Abelson, Greene, Appl. Phys. Lett. 69, 3869 (96),



GS-MBE Si(001):B

$T_s = 550\text{ }^\circ\text{C}$

θ (ML)

$$\frac{\theta_B}{C_B} = \frac{1-\theta_B}{1-C_B} \exp\left(\frac{-\Delta H_s}{kT_s}\right)$$

$$\theta_{\text{sat}, B} = 0.5\text{ ML}$$

$$\Delta H_s = -0.53\text{ eV}$$

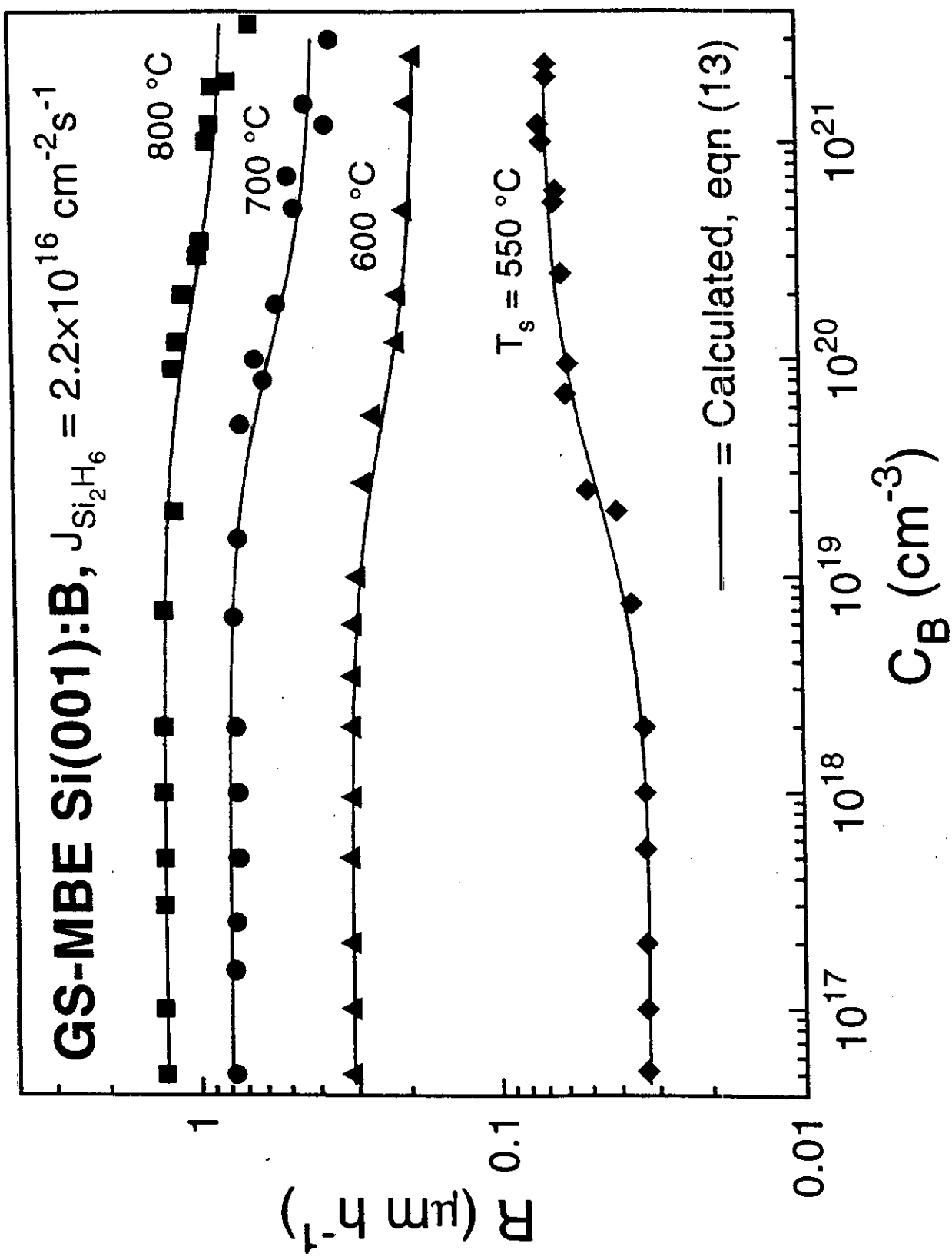
■ Experimental results
— Calculated, eqn. (8)

C_B (cm⁻³)

10^{18} 10^{19} 10^{20} 10^{21}

Kim, Glass, Gohla, Taylor, Park, Abelson, Greene, J. Appl. Phys. 84, 1077 (1997)

$$R_{Si} = \frac{2.5 \text{ Si}_2\text{H}_6 J_{\text{Si}_2\text{H}_6} \Theta_{db}^2}{n_{Si}} \quad \text{where: } \Theta_{db} = f_{ctn}(f, f^*, C_B, \Theta_B)$$



GS-MBE/UHV-CVD Si(001) : B
Growth Kinetics ($\text{Si}_2\text{H}_6/\text{B}_2\text{H}_6$)

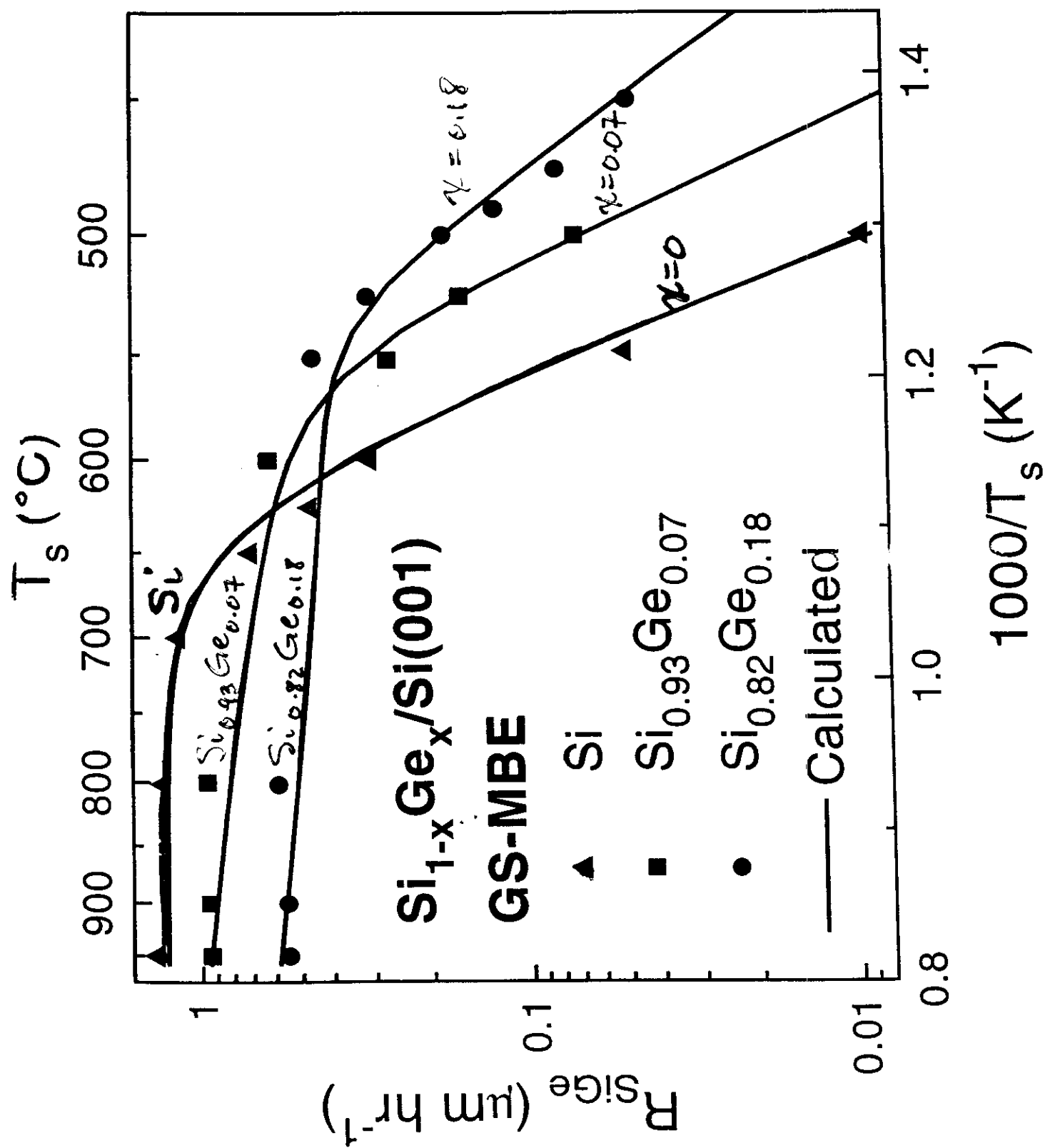
$$R_{\text{Si}} = \frac{2T_{\text{Si}_2\text{H}_6} S_{\text{Si}_2\text{H}_6} \theta_{\text{db}}^2}{N_{\text{Si}}} ; \quad \boxed{R_{\text{Si}} \propto \theta_{\text{db}}^2}$$

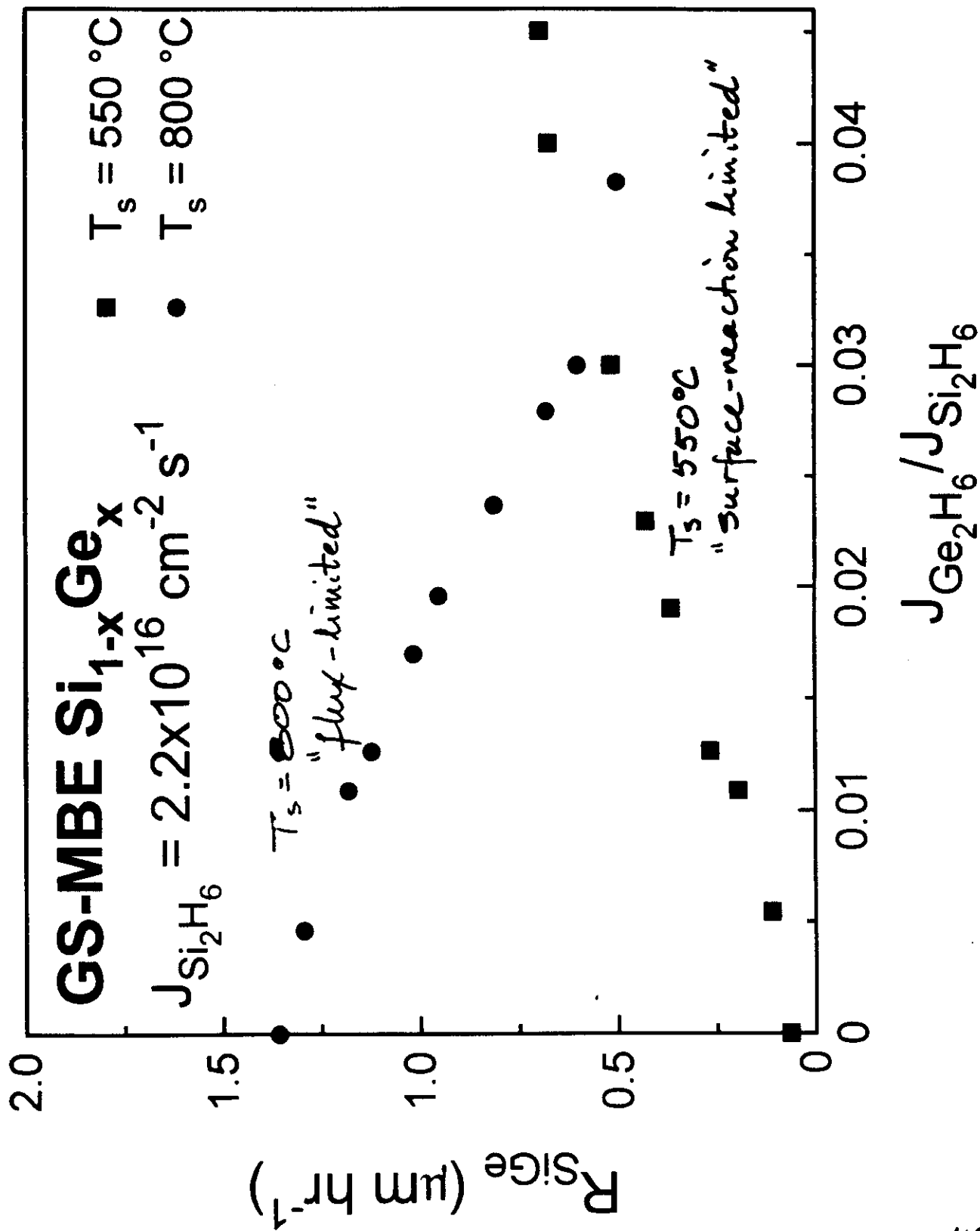
At $C_B \approx 1 \times 10^{19} \text{ cm}^{-3}$:

- $\theta_{\text{db}} \downarrow$ due to
 - * Si dimer vacancies.
 - * deactivation of Si_{db}^* ($\approx 1 \text{ db}/\text{Si}_2^*$).
- But, $E_{\text{d},\text{H}_2} \downarrow$ due to
 - * weakening of $\text{H}-\text{Si}^*$ bonds caused by Si^*-B backbond charge transfer and increased strain.

Thus:

- In the flux-limited (hi T_s) growth mode
 - * $\theta_{\text{H}} \rightarrow 0$
 - * $\therefore R_{\text{Si}} \downarrow$ since $\theta_{\text{db}} \downarrow$
- In the surface-reaction (lo T_s) growth mode
 - * θ_{H} is large
 - * $\therefore R_{\text{Si}} \uparrow$ since net $\theta_{\text{db}} \uparrow$





Calculating gas-source $\text{Si}_{1-x}\text{Ge}_x$ growth rates requires:

$$\begin{matrix} S_{\text{Si}_2\text{H}_6}(\theta_{\text{Ge}}, T_s) \\ S_{\text{Ge}_2\text{H}_6}(\theta_{\text{Ge}}, T_s) \end{matrix} \left\{ \begin{matrix} S_{\text{Si}_2\text{H}_6}^{\text{Si}}, S_{\text{Si}_2\text{H}_6}^{\text{Ge}} \\ S_{\text{Ge}_2\text{H}_6}^{\text{Si}}, S_{\text{Ge}_2\text{H}_6}^{\text{Ge}} \end{matrix} \right.$$

$$\frac{\theta_{\text{Ge}}(x, T_s)}{\theta_{\text{H}}(x, T_s)} > \Delta H_{\text{S,Ge}} [\theta_{\text{H}}(x, T_s)]$$

$$E_{\text{Si}}^{\text{H}}(\theta_{\text{Ge}})$$

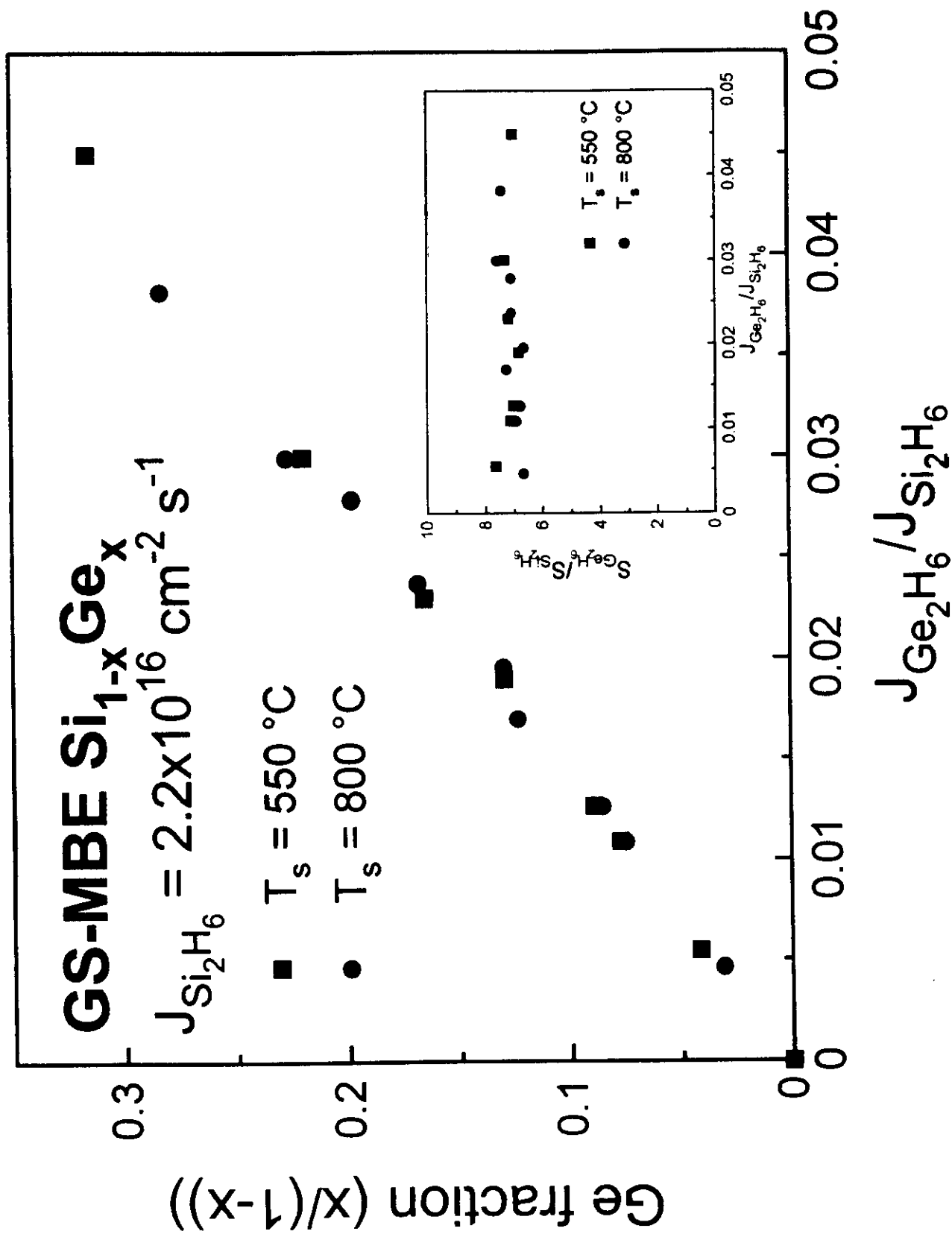
$$E_{\text{Ge}}^{\text{H}}(\theta_{\text{Ge}})$$

$$f_{\text{Si,db}}(x, \theta_{\text{Ge}}, T_s)$$

$$f_{\text{Ge,db}}(x, \theta_{\text{Ge}}, T_s)$$

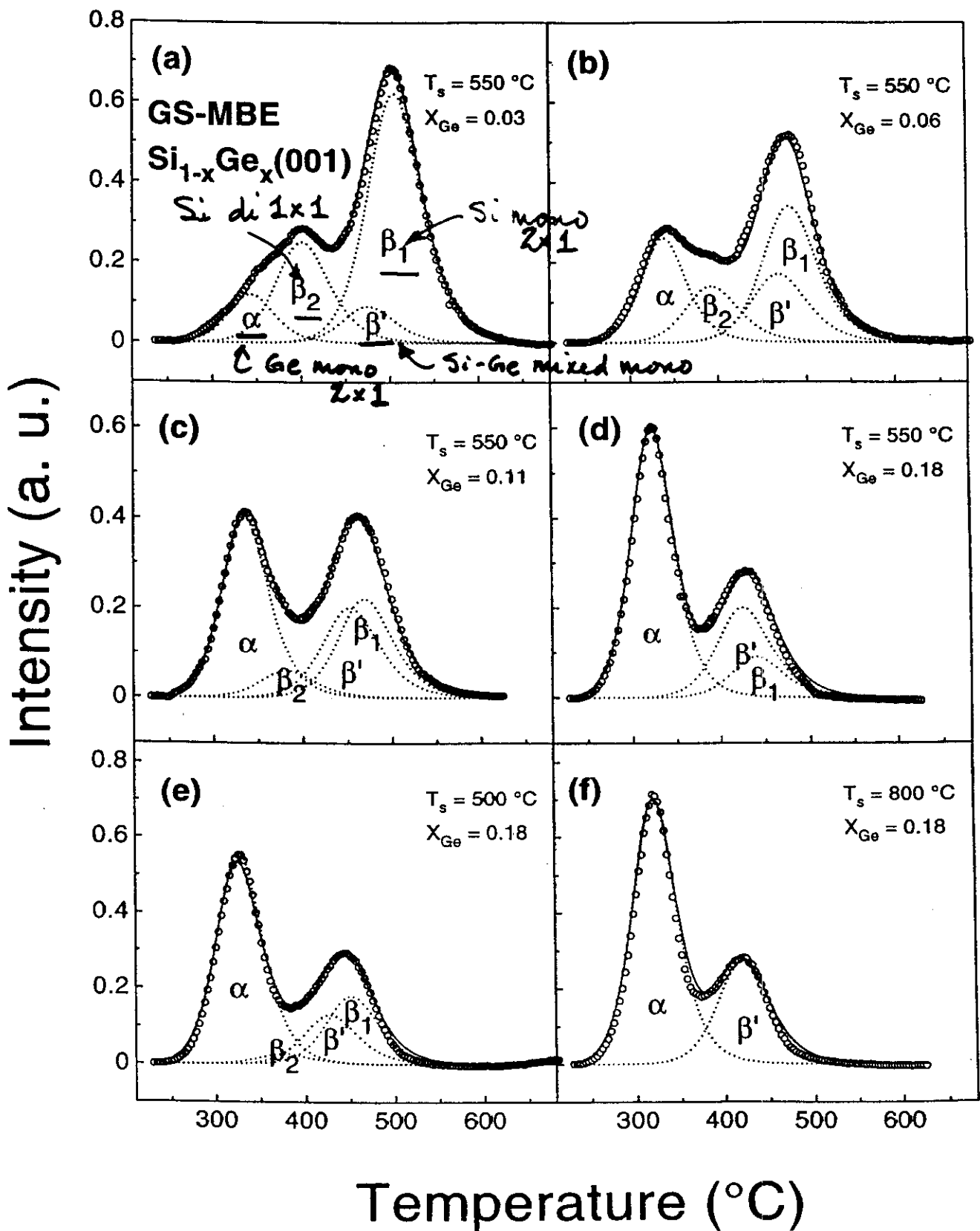
Knowledge of H desorption pathway from SiGe

Kinetic order of all adsorption, surface decomposition, and desorption steps



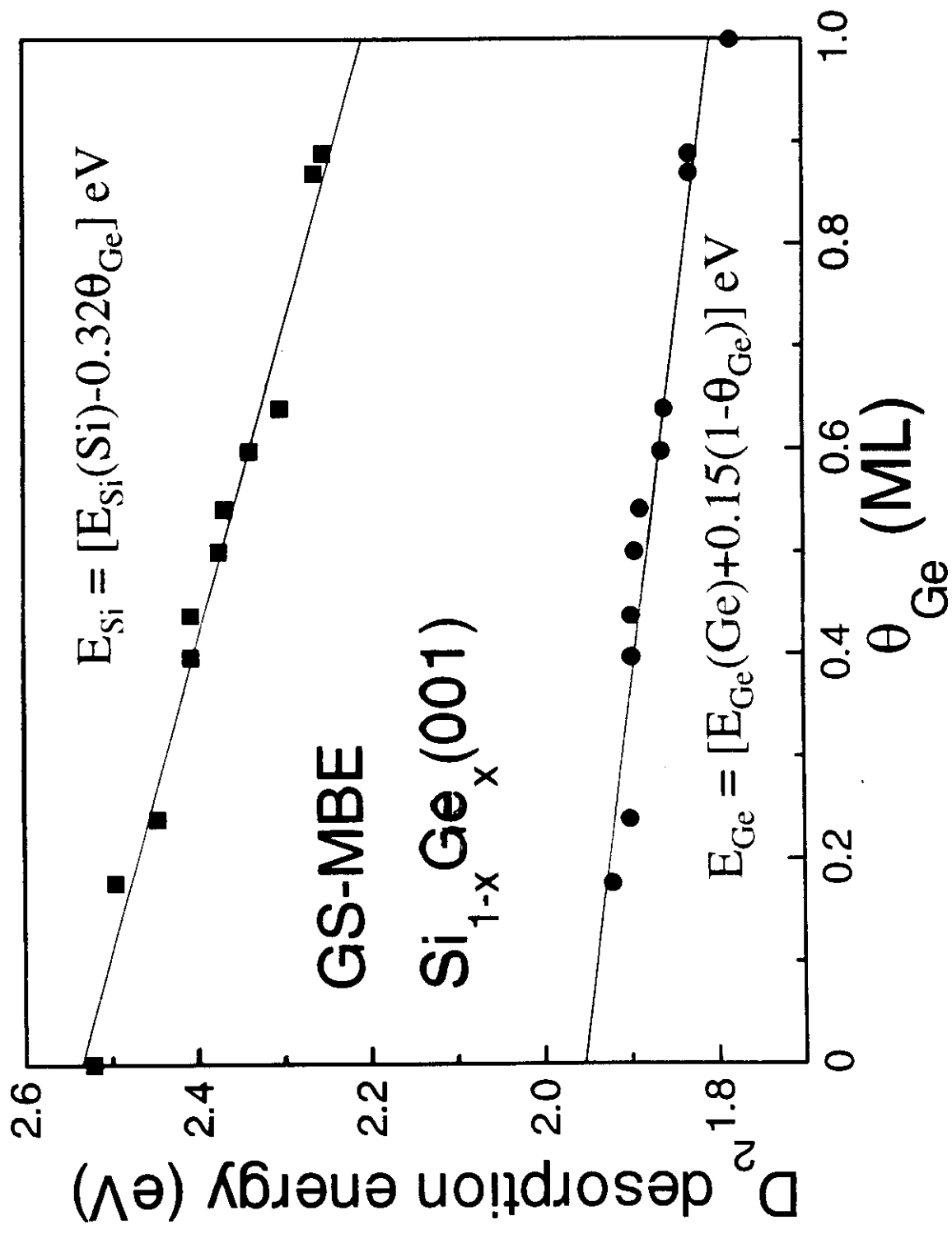
β_1 = Si monodeuteride, 2×1
 β_2 = Si dideuteride, 1×1

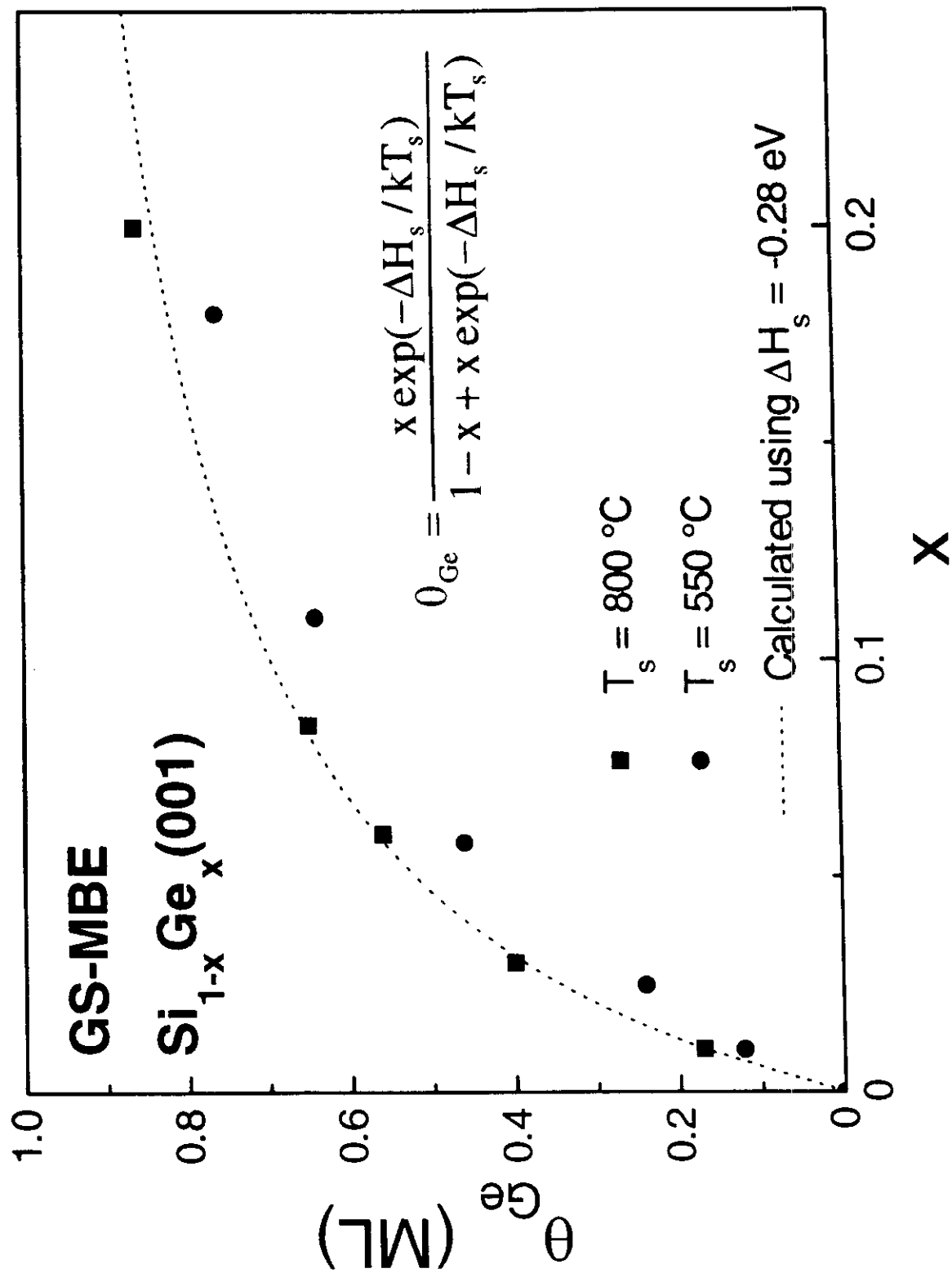
β' = Ge-Si monodeuteride
 α = Ge monodeuteride

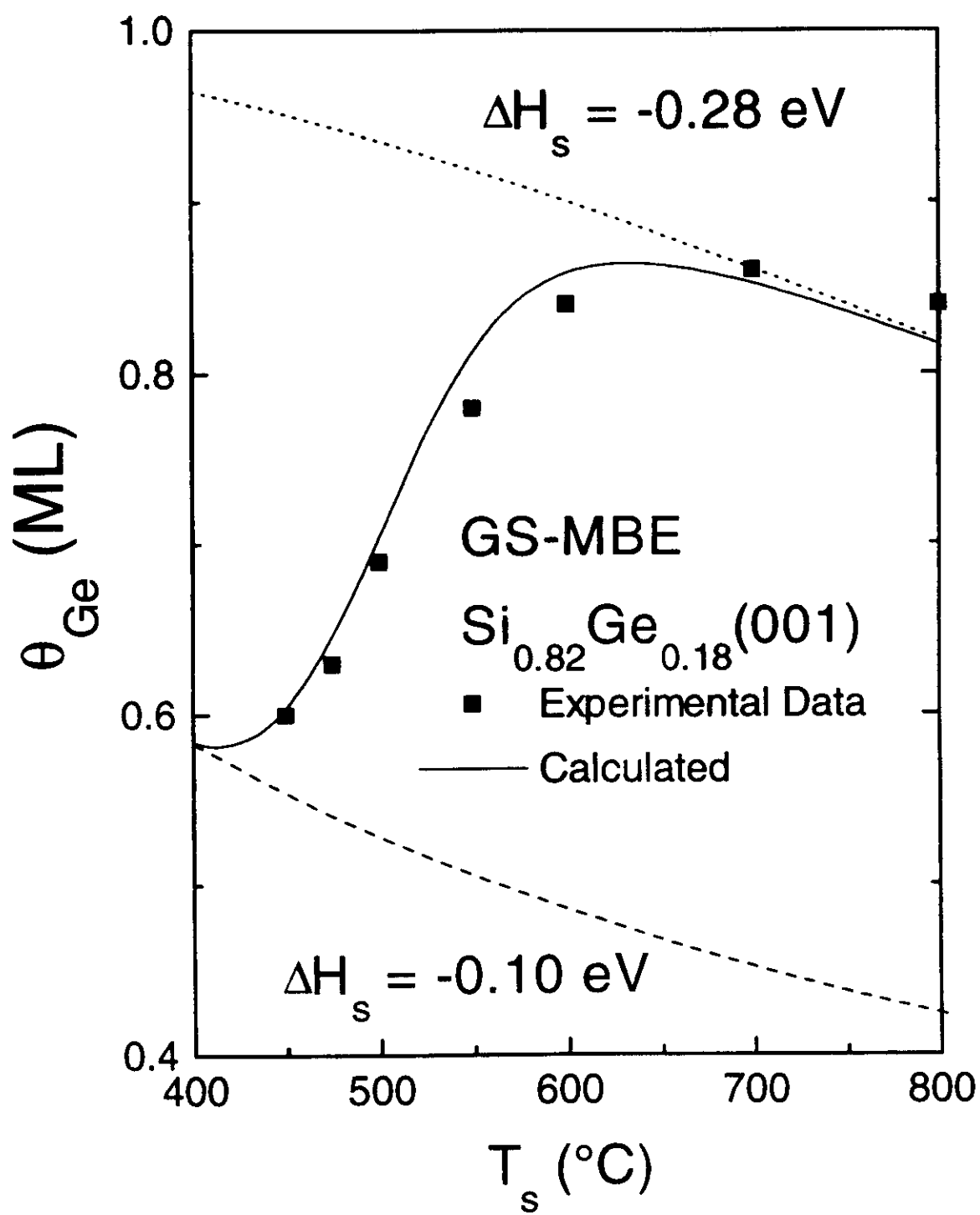


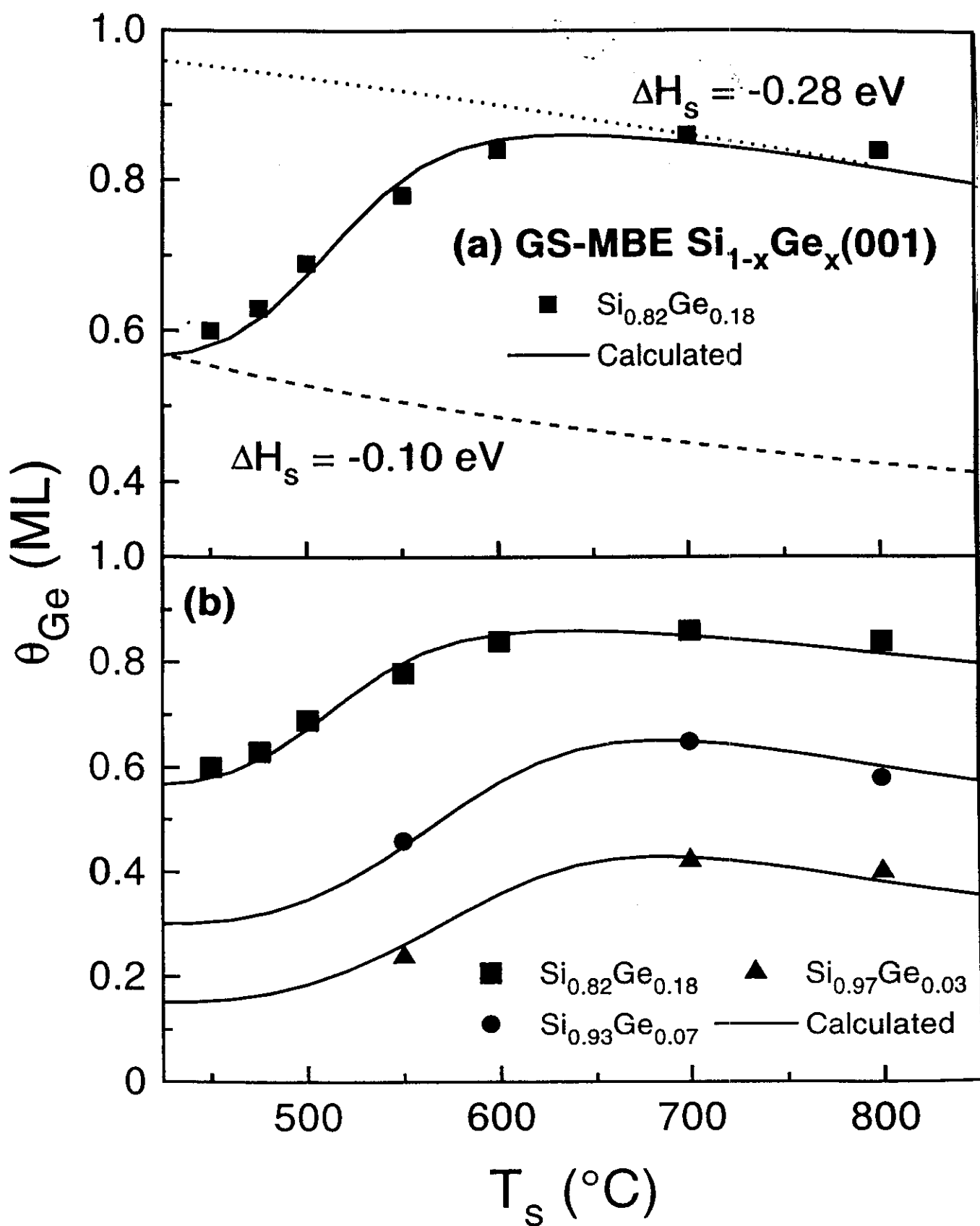
$$I_{\beta_1} + I_{\beta'_1} + I_{\alpha} = \text{constant} \Rightarrow r_{\text{Si}} \text{ (i.e. fully-strained)}$$

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Gas-source $\text{Si}_{1-x}\text{Ge}_x$ growth rate

$$R_{\text{Si,Ge}} = \frac{2\theta_{\text{Si}} f_{\text{db, Si}}^2}{N_{\text{Si,Ge}}} \left(J_{\text{Si}_2\text{H}_6} S_{\text{Si}_2\text{H}_6}^{\text{Si}} + J_{\text{Ge}_2\text{H}_6} S_{\text{Ge}_2\text{H}_6}^{\text{Si}} \right) + \frac{2\theta_{\text{Ge}} f_{\text{db, Ge}}^2}{N_{\text{Si,Ge}}} \left(J_{\text{Si}_2\text{H}_6} S_{\text{Si}_2\text{H}_6}^{\text{Ge}} + J_{\text{Ge}_2\text{H}_6} S_{\text{Ge}_2\text{H}_6}^{\text{Ge}} \right)$$

$$\theta_{\text{Ge}} = f_{\text{Si,db}} \left(\frac{x \exp(-\Delta H_S^1/kT_s)}{1-x+x \exp(-\Delta H_S^1/kT_s)} \right) + (1-f_{\text{Si,db}}) \left(\frac{x \exp(-\Delta H_S^2/kT_s)}{1-x+x \exp(-\Delta H_S^2/kT_s)} \right) \left\{ \begin{array}{l} \text{where!} \\ \Delta H_S^1 = -0.28 \text{ eV} \\ \Delta H_S^2 = -0.10 \text{ eV} \end{array} \right.$$

$$\theta_{\text{Ge}} + \theta_{\text{Si}} = 1$$

$$f_{\text{Si,db}} = \left[1 + \frac{\sqrt{2 J_{\text{Si}_2\text{H}_6} S_{\text{Si}_2\text{H}_6}^{\text{Si}}}}{N_{\text{Si,Ge}} \frac{1}{2} \exp(-E_{\text{Si}}^H/kT_s)} \right]$$

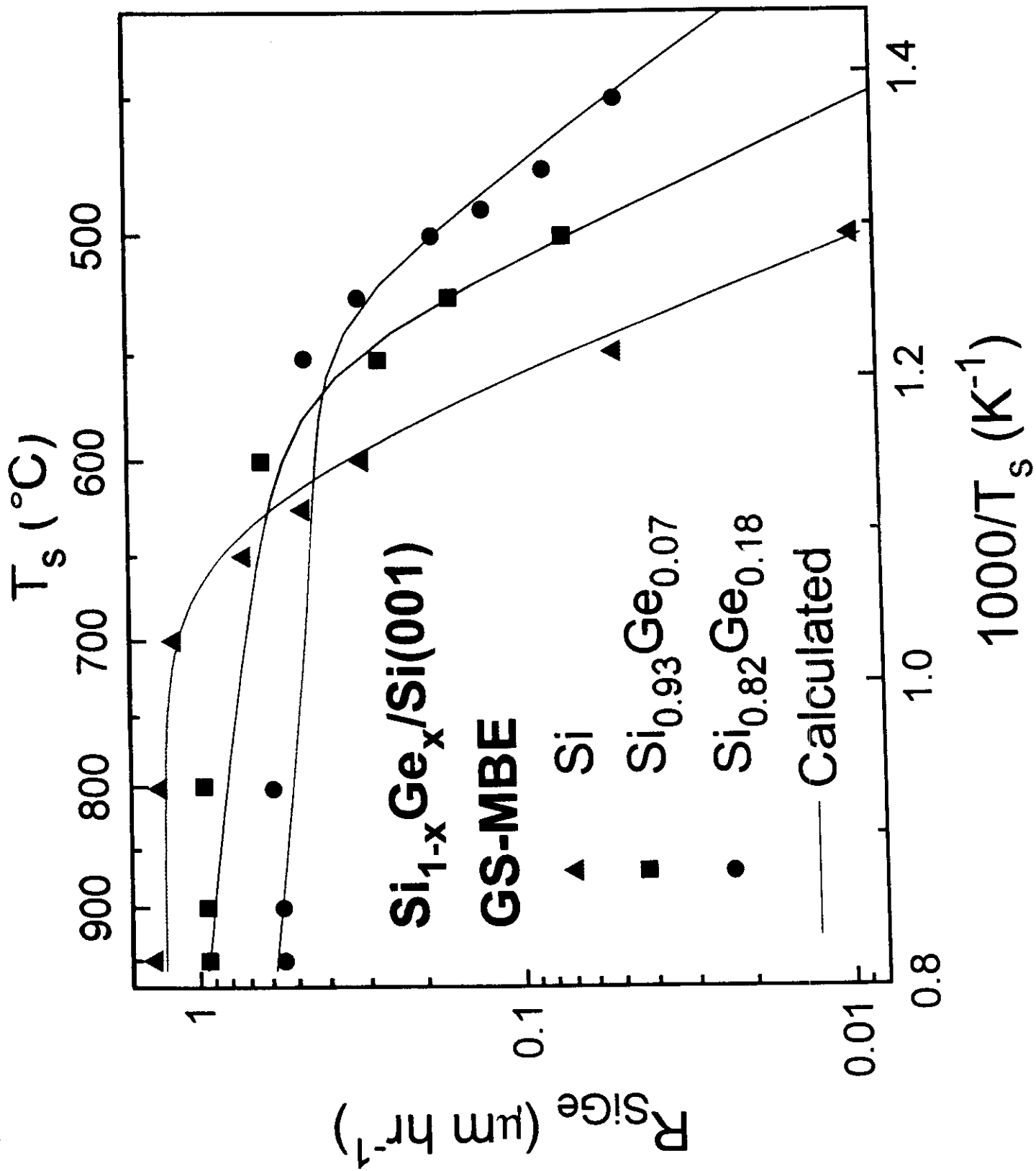
$$f_{\text{Ge,db}} = \left[1 + \frac{\sqrt{2 J_{\text{Ge}_2\text{H}_6} S_{\text{Ge}_2\text{H}_6}^{\text{Ge}}}}{N_{\text{Si,Ge}} \frac{1}{2} \exp(-E_{\text{Ge}}^H/kT_s)} \right]$$

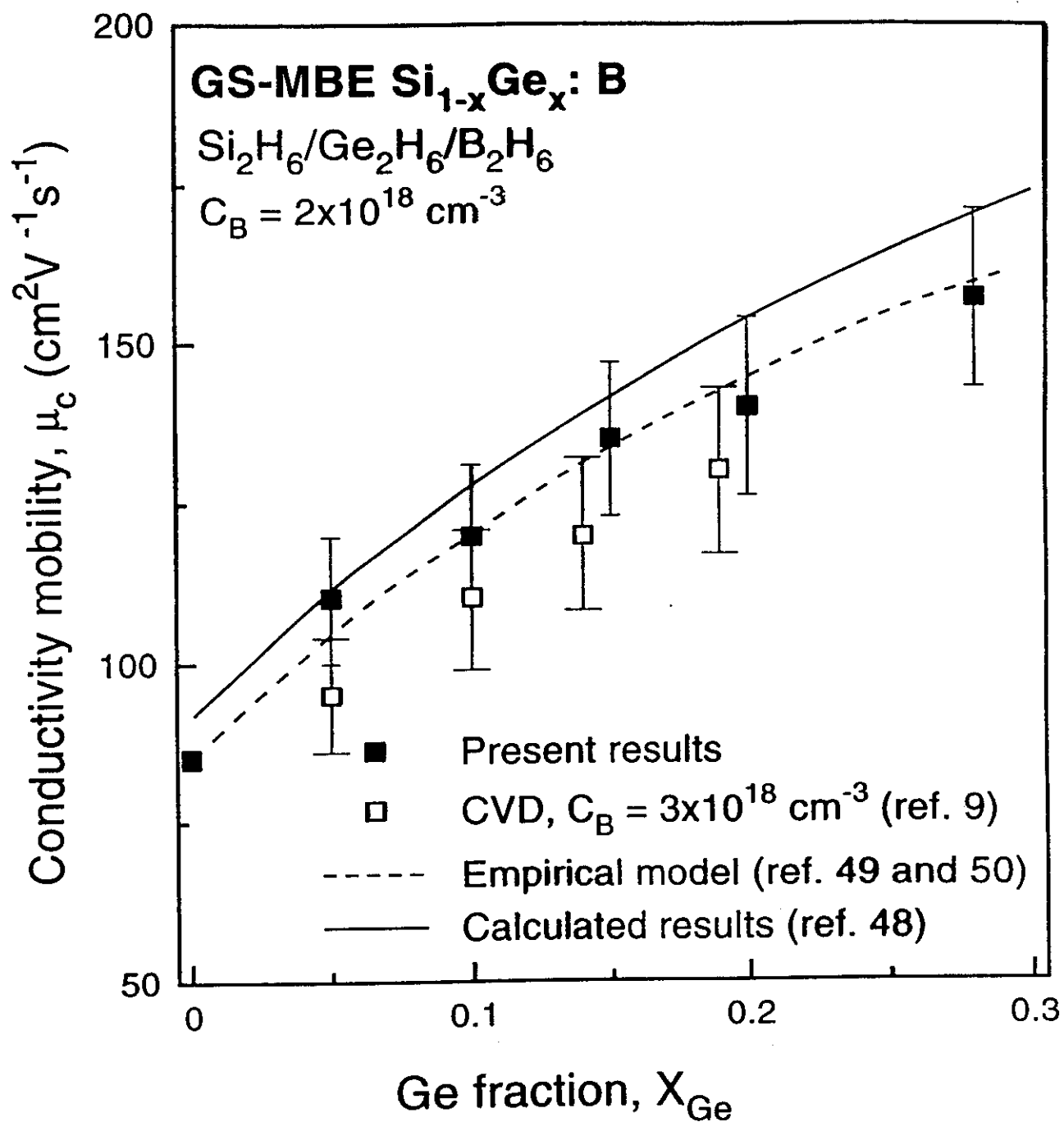
$$E_{\text{Si}}^H = [2.52 - 0.32 \theta_{\text{Ge}}]$$

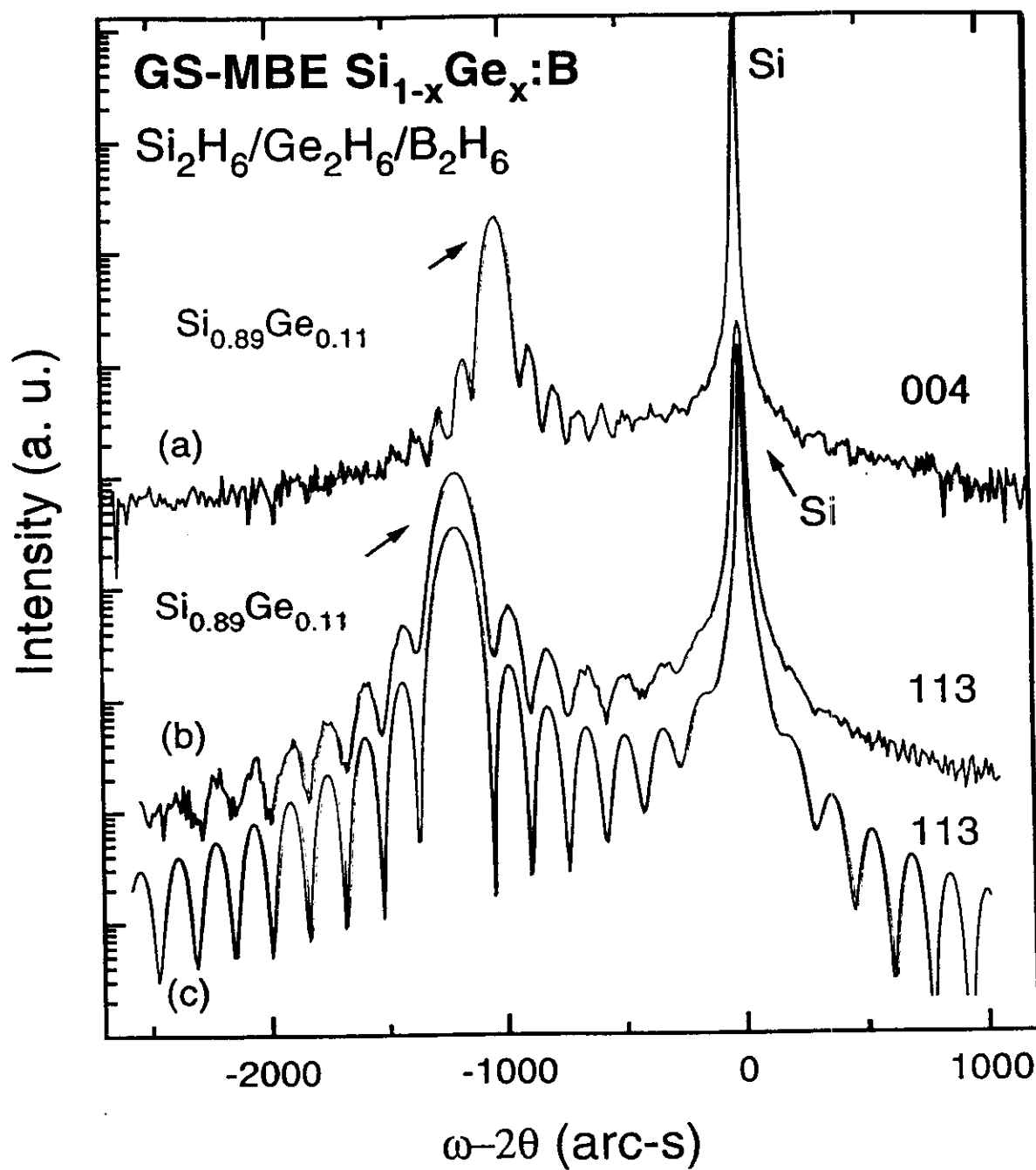
$$E_{\text{Ge}}^H = [1.80 + 0.15 (1 - \theta_{\text{Ge}})]$$

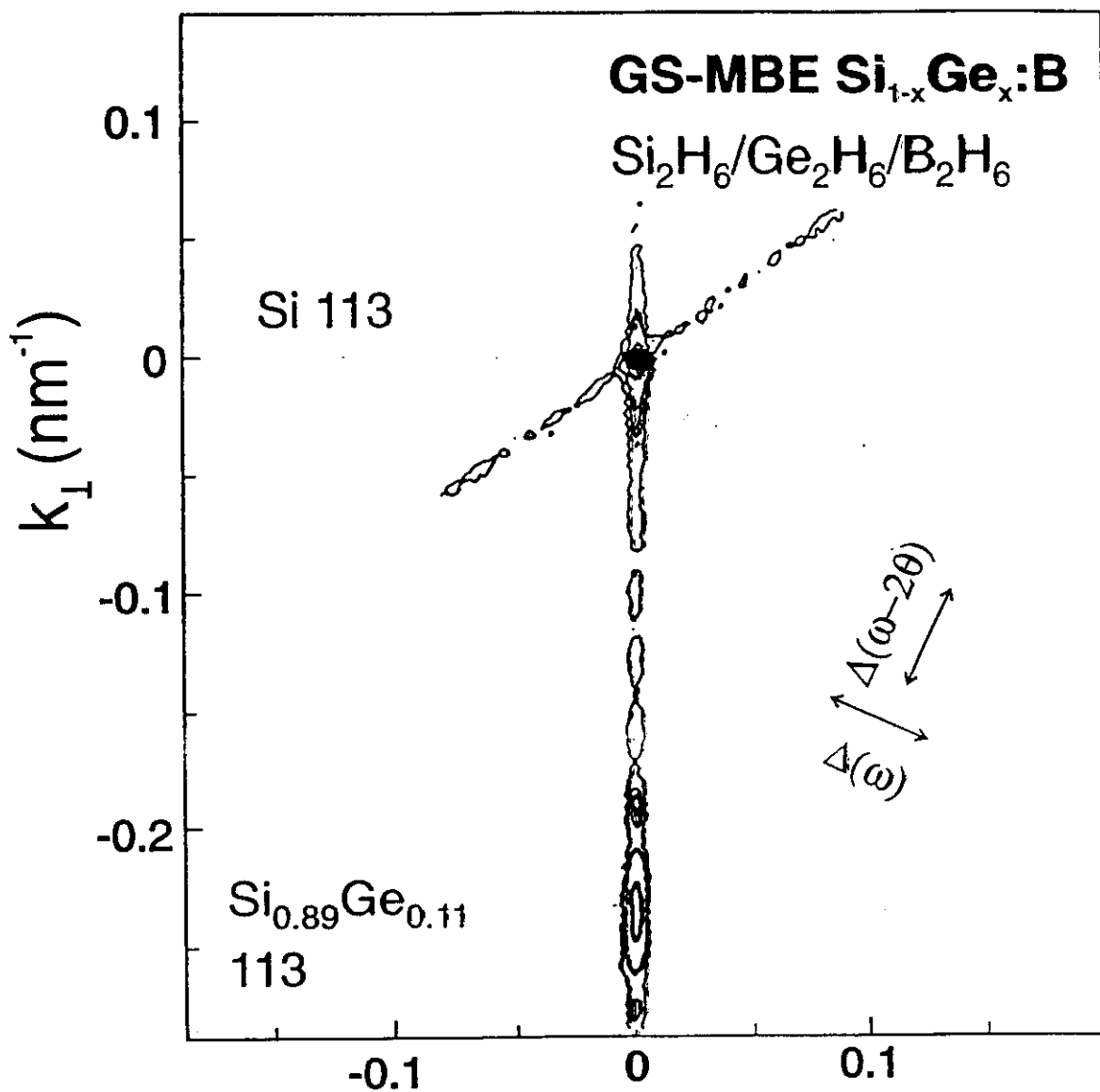
$$S_{\text{Si}_2\text{H}_6} = \theta_{\text{Si}} S_{\text{Si}_2\text{H}_6}^{\text{Si}} + \theta_{\text{Ge}} S_{\text{Si}_2\text{H}_6}^{\text{Ge}}$$

$$S_{\text{Ge}_2\text{H}_6} = \theta_{\text{Ge}} S_{\text{Ge}_2\text{H}_6}^{\text{Ge}} + \theta_{\text{Si}} S_{\text{Ge}_2\text{H}_6}^{\text{Si}}$$





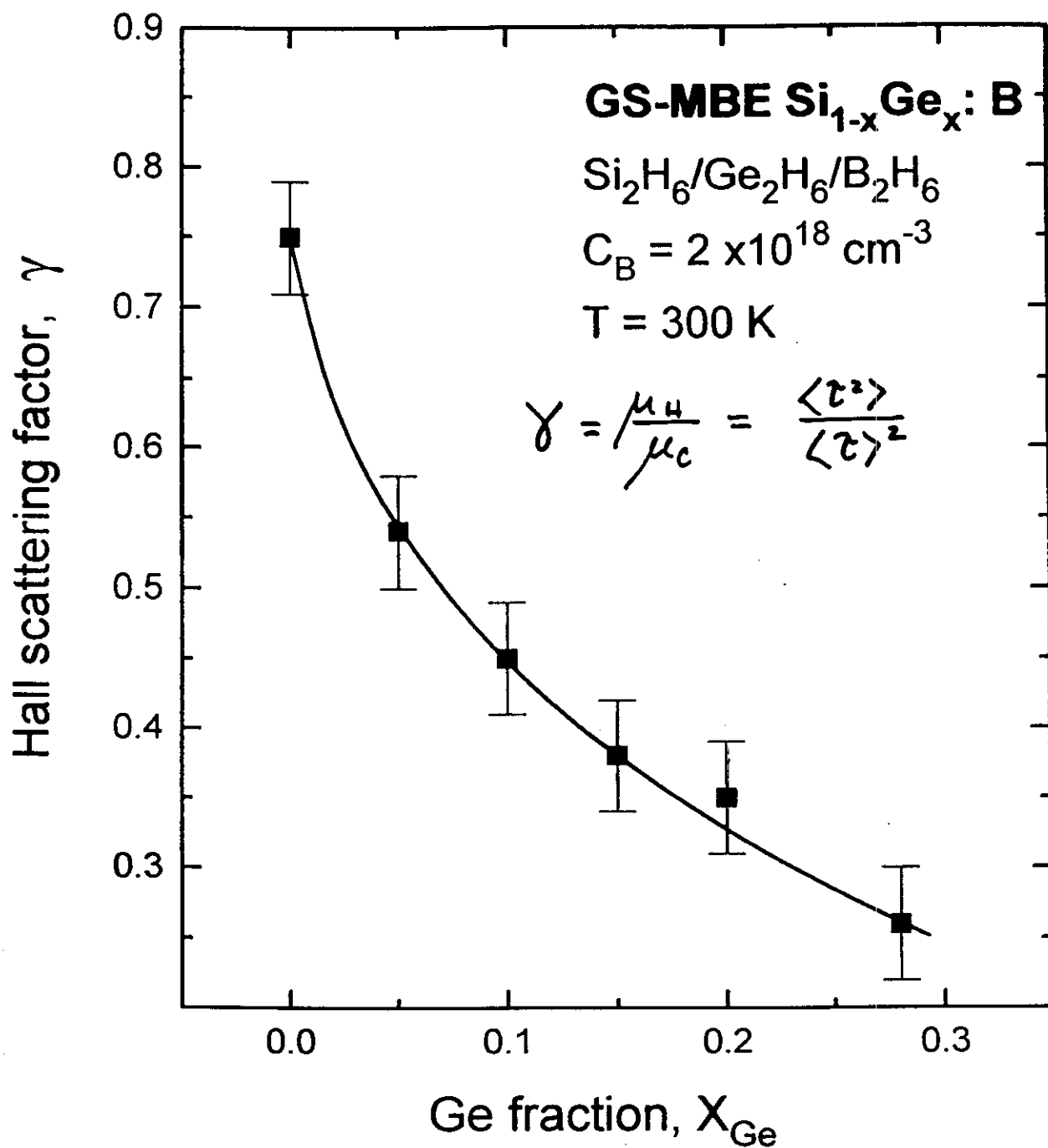


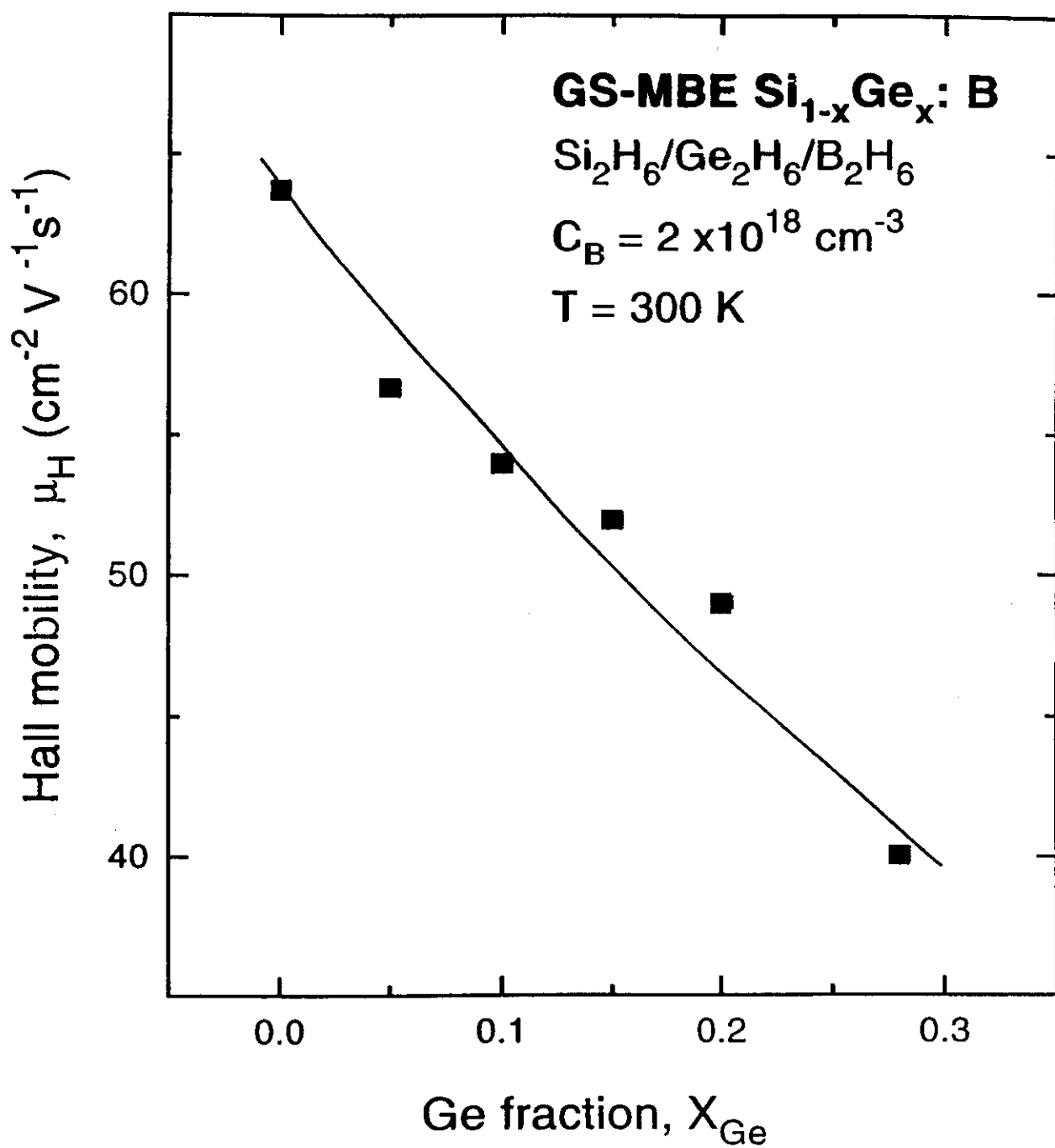


$$a_{\parallel, \text{SiGe}} = 0.54312 \pm 0.00002 \text{ nm}$$

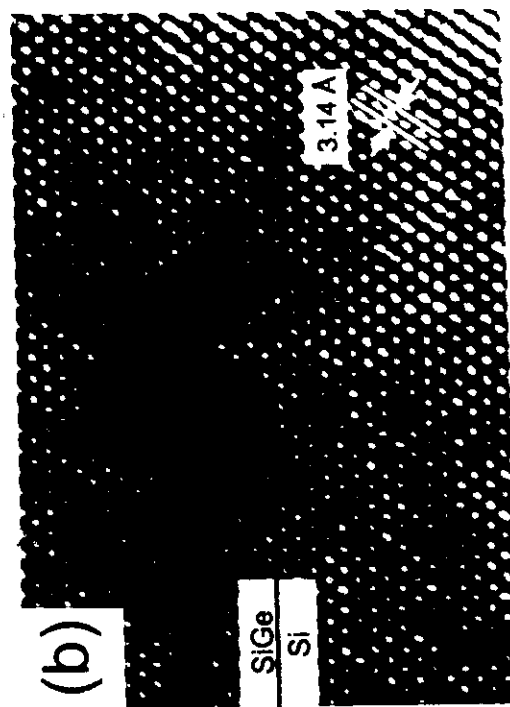
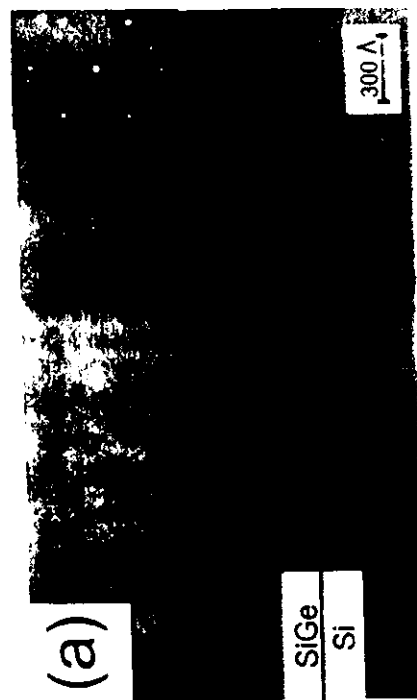
$$\therefore \frac{\Delta a}{a_{\text{Si}}} \leq 4 \times 10^{-5} !$$

$$\Gamma_{\parallel} = 24.5 \text{ arc-s}, \Gamma_{\omega} = 24.9 \text{ arc-s}, \Gamma_{\omega-2\theta} = 24.7 \text{ arc-s}$$





GS-MBE $\text{Si}_{1-x}\text{Ge}_x/\text{Si}(001)$



$$X = 0.18, T_s = 500\text{ }^{\circ}\text{C}$$