Open access • Journal Article • DOI:10.1063/1.3054643

Effect of temperature on layer separation by plasma hydrogenation

Zengfeng Di, Yongqiang Wang, M. Nastasi, F. Rossi ...+2 more authors

Published on: 22 Dec 2008 - Applied Physics Letters (American Institute of Physics)

Topics: Hydrogen

LA-UR- 08-7531

Approved for public release; distribution is unlimited.

Title:

Effect of temperature on layer separation by plasma-hydrogenation

Author(s):

Zengfeng Di, [a] Yongqiang Wang, Michael Nastasi,
Los Alamos National Laboratory, Los Alamos, New Mexico, 87545, USA
Francois Rossi
Joint Research Centre, European Commission, 21020 Ispra(Va), Italy
Lin Shao
Department of Nuclear Engineering, Texas A&M University, 3133 TAMU, College Station, Texas, 77843, USA
Phillip E. Thompson
Code 6812, Naval Research Laboratory, Washington, DC 20375-5347

Intended for:

Publication in Applied Physics Letters

Effect of temperature on layer separation by plasma-hydrogenation

Zengfeng Di, [a] Yongqiang Wang, Michael Nastasi,

Los Alamos National Laboratory, Los Alamos, New Mexico, 87545, USA

Francois Rossi

Joint Research Centre, European Commission, 21020 Ispra(Va), Italy

Lin Shao

Department of Nuclear Engineering, Texas A&M University, 3133 TAMU, College Station, Texas, 77843, USA

Phillip E. Thompson

Code 6812, Naval Research Laboratory, Washington, DC 20375-5347

Abstract

We have studied the behavior of hydrogen diffusion in plasma hydrogenated Si/SiGe/Si heterostructure at different temperatures. At low temperature, the intrinsic point defects present in the MBE grown Si capping layer are found to compete with the buried strain SiGe layer for hydrogen trapping. The interaction of hydrogen with point defects affects the long-range diffusion of hydrogen, and restricts the amount of hydrogen available for trapping by the strain SiGe layer. However, hydrogen trapping by the capping layer is attenuated with increasing hydrogenation temperature, which is due to the instability of vacancy-hydrogen point defects. More hydrogen trapping in the strain SiGe layer occurs and subsequent surface blister formation is realized in the absence of trap-limited diffusion. A potential temperature window for plasma hydrogenation induced layer separation and transfer is identified based on the combined considerations of trap-limited diffusion occurring at low temperature and out-diffusion of H_2 molecule together with the dissociation of Si-H bonds inside of H platelet occurring at high temperature.

PACS: 52.77Dq; 78.30-j; 61.72j-; 66.30.-h

Keywords: Plasma-hydrogenation; Infrared spectroscopy; Point defects; Diffusion

[a] Corresponding author:

Dr. Zengfeng DI

Telephone: 505-665-4995

Fax: 505-667-8021

Email: dizengfeng@hotmail.com

The diffusion of hydrogen in Si is influenced by a number of phenomena.[1] Atomic hydrogen can exist in several charge states (notably H^+ in p-type material and H^- or H^0 in n-type materials),[2] making it susceptible to trapping by dopants, impurities, and lattice defects during its diffusion through the lattice.[3-5] Diffusion can also be influenced by hydrogen-hydrogen interaction. (e.g., molecular hydrogen H_2 and dimer (H_2^*) formation[6]). These interactions will have a strong influence on the movement of hydrogen through the lattice, producing anomalous features in hydrogen diffusion profiles, and making it very difficult or even impossible to determine the intrinsic diffusivity D_i of free atomic hydrogen, especially at low temperature when trapping effect due to these interactions is significant.

Van Wieringen and Warmoltz (VWW) examined H diffusion in Si at high temperatures (~1240 – 1400 K) using permeation measurements,[7] and observed an Arrhenius temperature dependence: $D_i(T)=D_0\exp(-E_A/k_BT)$, where $D_0=9.41\times10^{-3}\text{cm}^2\text{s}^{-1}$ and $E_A=0.48$ eV (activation energy). The parameters obtained by VWW are considered as the intrinsic H diffusion coefficient since the experiment temperatures used ensured minimal interactions with impurities, dopants, or defects. At lower temperatures, diffusion measurements showed a departure from the VWW extrapolation[8] with significant increases in D_0 and E_a. This was attributed to the onset of trap-limited diffusion due to chemical reactions between diffusing H and lattice impurities and defects in the material.[9,10]

Our recent studies on strain facilitated layer transfer,[11-14] which depends on hydrogen diffusion through an MBE grown Si surface layer to a buried strain layer, showed that successful exfoliation was only achieved above a certain temperature. Since trap-limited diffusion is temperature dependent, it was hypothesized that vacancy type defects present in our MBE grown films served as trapping sites to retard the diffusion of H into the strain layer, thereby inhibiting exfoliation at lower temperatures.[15] The present work is devoted to investigating the interaction between the diffusing H with the vacancy type defects in Si/SiGe/Si heterostructures, and further exploring the mechanism underlying this temperature dependent exfoliation phenomenon.

Si/$Si_{0.80}Ge_{0.20}$/Si heterostructures were synthesized by molecular beam epitaxy (MBE). A 5-nm-thick epitaxial $Si_{0.80}Ge_{0.20}$ layer was grown on a (100) Si substrate followed by a 150-nm-thick crystalline Si layer at 650 °C. The samples were subsequently hydrogenated for 0.5-2 h, in a distributed electron cyclotron resonance plasma reactor with a low frequency (2 kHz) bias of approximately -100 V. Since vacancy-hydrogen point defects are stable up to 250 °C,[16] hydrogenation experiments were performed at 250 °C (low temperature) and 300 °C (high temperature) for comparison. Depth distributions of hydrogen were measure by elastic recoil detection (ERD) and secondary ion mass spectrometry (SIMS). ERD analysis was performed using a 1.5MeV $4He^+$ beam oriented 75 ° from the sample normal, with the detector positioned 150 ° away from the incident beam. SIMS measurements were performed using 1 keV Cs^+ beam. Multiple internal reflection infrared spectroscopy (MIR-IR) was used to monitor the evolution of hydrogen related defects. The surface morphology after hydrogenation was characterized by scanning electron microscopy (SEM).

Table 1 summarizes the SEM observations of the Si/$Si_{0.80}Ge_{0.20}$/Si samples after hydrogenation at 250 °C and 300 °C for various durations. Blistering is observed for all hydrogenation exposures at 300 °C. The mean blister diameter is found to increase with increasing hydrogenation time, while the density of the surface blisters decreases correspondingly. At the longest hydrogenation time of 2 hr exfoliated blisters are observed. In contrast, the blistering kinetics are very different when hydrogenation is performed at 250 °C. As this temperature surface blisters are only observed after a 2 h exposure; surfaces blisters could not be observed by SEM for samples treated less than 2 h.

Fig. 1(a) shows hydrogen and germanium profiles obtained from the Si/$Si_{0.80}Ge_{0.20}$/Si samples hydrogenated for 1 h at 250 °C and 300 °C using SIMS. The hydrogen distributions measured by

ERD, are shown in Fig. 1 (b). Hydrogen diffusion profiles along with H trapping at the strained SiGe buried layer are observed for both measurement methods. Furthermore, the SIMS data clearly shows that hydrogen has accumulated throughout the Si capping layers, with greater accumulation at 250 °C. It should be noted that SIMS is insensitive to H_2 since it is noncharged, not bound to Si dangling bonds, and will easily out-diffuse as sputter erosion exposes previously buried H_2 to vacuum,[17,18] so the total amount of hydrogen trapped in the buried SiGe layer is better characterized by ERD (Fig. 2(b)), which is independent of the chemical form (atomic or molecular) of hydrogen. The ERD data shows that there is more hydrogen trapped in the buried SiGe layer, while less hydrogen is present in the capping Si layer (as indicated by shadowing in Fig. 2 (b)) when the isochronal hydrogenation is performed at 300 °C.

The chemical nature of the retained H is given by IR measurements. Fig. 2 compares the IR data from the plasma hydrogenated Si/SiGe/Si samples at 250 °C and 300 °C for 1 h; Si-H bond stretching modes have been labeled. Four discrete modes can be observed on the continuous band from 2063cm^{-1} to 2113cm^{-1} that are attributed to the presence of H (111) and (100) platelets. The mode at 2063 and 2082cm^{-1} are assigned to the Si-H bonds at Si (111) internal surface.[19,20] The mode at 2105cm^{-1} is due to the perturbed symmetric stretching mode of a coupled monohydride species $(SiH)_2$ on atomically smooth Si (100) surface, and the mode at 2113cm^{-1} is assigned to the asymmetric dihydride stretching motion SiH_2 on atomically rough Si (100) surface.[21,22] Platelets with a (111) orientation have been observed by many researchers to readily formed in the near-surface region of plasma treated Si,[23,24] while the formation of (100) platelets has been attributed to hydrogen interaction with vacancy type defects in a region of in-plane compressive stress.[25, 26] In addition to Si-H modes associated with platelets, three discrete modes corresponding to H-defect complexes are also observed after plasma hydrogenation at 250 °C, but not in the sample hydrogenated at 300 °C. The mode at 2147 cm^{-1} has been previously assigned to double hydrogen atoms bound to a monovacancy defect (VH_2) and the bands at 2166 and 2182cm^{-1} are due to three hydrogen atoms bound to the monovacancy (VH_3) or six hydrogen atoms bound to the divacancy (V_2H_6).[21, 22] (It should be noted that VH_3 and V_2H_6 have the same structure and symmetry in vibration, are hardly distinguishable experimentally and theoretically.)[27]

A comparison of the data in Fig 2 shows the intensity of the absorption peaks corresponding to Si-H bonds in platelets are enhanced and the peaks corresponding to hydrogen-vacancy point defects are significantly reduced following 300 °C hydrogenation, relative to 250 °C hydrogenation. Considering the reduced concentration of hydrogen in the buried SiGe layer and corresponding increased hydrogen content in the Si capping layer when the hydrogenation is performed at 250 °C, as shown in Fig. 1 (a) and (b), the extra IR peaks corresponding to 2147, 2166 and 2182 cm^{-1} are most probably due to vacancy-hydrogen defects formed in the capping Si layer. The combined data presented in Figs. 1 and 2 suggests the Si capping layer greatly affects H diffusion to, and accumulation in the buried strain layer, and that the distribution of H in the Si/SiGe/Si sample after hydrogen plasma treatment is dependent on the hydrogenation temperature.

It is well know that the dominant defects in low temperature MBE grown films are vacancies, which are caused by limited adatom mobility on the epitaxial surface. [28, 29] The net effect of the vacancies during hydrogenation is to act as traps that mediate the diffusion of H, which in turn decreases the H flux at the strain layer. However, the stability of H related vacancy defects or pure vacancy defects are temperature dependent. Annealing studies show that vacancy-H defects such asVH and VH_2 can exist below 240 °C and the divacancy is stable below 270 °C. [16] Therefore, it is anticipated that H trapping in the capping Si layer should be significantly decreased when hydrogenation is executed at higher temperature, consistent with our findings. The instability of H related vacancy defects at high temperature is verified by the FTIR data presented in Fig. 3, which shows the results from the vacuum annealing of a sample previously hydrogenated at 250 °C . These data show that the H related vacancy defects formed during 250

°C hydrogenation are attenuated (as indicated by shadowing) after annealing at 300 °C for 4 h, which is higher than the threshold dissociation temperature for most vacancy-hydrogen defects,. However, what is significant about this data is the persistence of modes corresponding to H in (111) or (100) platelets at 300 °C , which are responsible for the development of H-decorated internal surfaces necessary for blister formation. The attenuation of vacancy-hydrogen point defects and the persistence of platelets after annealing at 300 °C implies that vacancy mediated trap-limited diffusion of hydrogen in capping Si layer will be less active when the hydrogenation is performed at 300 °C, thereby allowing hydrogen to reach the buried SiGe strain layer where stable (100) platelets can form, which ultimately evolve into surface blisters.

Weldon was among the first to use IR spectroscopy[19] to study blistering in H implanted Si. A significant observation from that work was that all important steps in the evolution of implanted hydrogen occur in the temperature range between 250 °C and 400 °C. In that temperature range, hydrogen atoms are librated from monohydride multivancancies (V_nH_m, $m \leq n$) and recaptured by monovancancies to form $V_1H_{3,4}$ defects that evolve into H-decorated internal surfaces. These flat cavities continue to capture hydrogen that ultimately react with each other to form H_2, which provides the internal pressure for crack propagation and blistering. Therefore, the formation of (100) H-decorated internal surfaces along with the continued diffusion of hydrogen to these features are the two key components needed for blister formation and surface cleavage Si subjected to ion implantation or hydrogenation. Previous work using forward recoil scattering (FRS)[19] and thermal desorption spectra (TDS)[30] showed the out diffusion of gaseous H_2 from hydrogen implanted Si above 400 °C. Furthermore, the FTIR data from the vacuum annealing of a sample previously hydrogenated at 250 °C in Fig. 3 shows a decrease in the Si-H stretch vibrations on H-decorated internal surface also occurs at 400 °C, which indicates the dissociation of Si-H bonds. Therefore, the continuous hydrogen trapping at a buried SiGe strain layer by the formation of H-decorated internal surfaces (platelets) and subsequent formation of H_2 molecules can only be achieved below a certain temperature, where the equilibrium between hydrogen out-diffusion and hydrogen trapping is reached.

The kinetic and trapping behavior of hydrogen in Si structures containing a buried SiGe strain layer and resultant blister formation have implications in the fabrication of SOI wafers. The key parameter for the ion-cut approach to SOI manufacturing is an ion implantation fluence window below or above which silicon cleavage cannot be generated.[30, 31] In the present study the total amount of trapped hydrogen responsible for surface blistering is dependent on temperature window of the plasma hydrogenation. Below the temperature window the intrinsic point defects present in the MBE grown Si capping layer are found to compete with the buried strain SiGe layer for hydrogen trapping thus inhibiting blister formation and the possibility of layer transfer. However, hydrogen trapping by the capping layer is attenuated with increasing hydrogenation temperature within the window, which is due to the instability of vacancy-hydrogen point defects. More hydrogen trapping in the strain SiGe layer occurs and subsequent surface blister formation is realized in the absence of trap-limited diffusion. One the other hand, at temperatures above this window H will dissociate from the defects within the strain layer and out-diffusion will result in the loss of hydrogen. Certainly, the hydrogen plasma density surrounding the specimen, which is quite relevant to several experiment parameters including microwave power and frequency, bias voltage, et al., also influences the amount of H available for in-diffusion, plays a role in this process. Therefore, the temperature window may be slightly variable depending plasma conditions. The relevance of this aspect is currently under investigation.

In summary, we have shown that the plasma hydrogenation temperature can significantly affect the H diffusion and accumulation behaviors in Si/SiGe/Si heterostructure. At low temperature, the interaction of diffusing H with the vacancy type defects in the Si capping layer impedes long-range H migration and trapping in the buried SiGe layer, which in turns affects surface blister formation. At higher temperatures dissociation of Si-H bonds on the H-decorated internal surfaces, i.e, H platelets, occurs leading to H out-diffusion. The optimum conditions for plasma hydrogenation induced layer transfer requires a hydrogenation temperature window where H diffusion can easily occur while still allowing for sufficient trapping and accumulation to produce the required internal pressures needed to promote crack propagation and layer separation.

Acknowledgements

This work is supported by the Department of Energy, Office of Basic Energy Science and by the Office of Naval Research.

References:

[1] S. J. Pearton, J. W. Corbett, and J. T. Borenstein, Physica B, 170, 85 (1991)

[2] C. Herring and N. M. Johnson, in Semiconductors and Semimetals, edited by J. I. Pankova and N. M. Johnson (Academic Press, San Diego, 1991), Vol. 34, Chap. 10.

[3] S. J. Pearton, J. W. Corbett, and M. Stavola, in Hydrogen in Crystalline Semiconductors, edit by H. J. Queisser (Springer-Verlag, New York, 1992), p. 200.

[4] S. J. Pearton, J. W. Corbett, and T. S. Shi, Appl. Phys. A 43, 153 (1987)

[5] N. M. Johnson, C. Doland, F. Ponce, J. Walker, and G. Anderson, Physica B 170, 3 (1991)

[6] J. D. Holbech, B. Bech Nielsen, R. Jones, P. Sitch and S. Öberg, Phys. Rev. Lett. 71, 875 (1993)

[7] A. Van Wieringen and N. Warmoltz, Physica (Utrecht) 22, 849 (1956)

[8] G. Panzarini and L. Colombo, Phys. Rev. B, 73, 1636 (1994)

[9] M. C. Wagener, J. R. Botha, and A. W. R. Leith, Phys. Rev. B, 60, 1752 (1999)

[10] T. Zundel and J. Weber, Phys. Rev. B, 46, 2071, (1992)

[11] Z. F. Di, Y. Q. Wang, M. Nastasi, F. Rossi, J. K. Lee, L. Shao, and P. E. Thompson, Appl. Phys. Lett. 91, 244101 (2007)

[12] L. Shao, Y. Lin, J. K. Lee, Q. X. Jia. Y. Q. Wang, M. Nastasi, P. E. Thompson, N. D. Theodore, P. K. Chu, T. L. Alford, J. W. Mayer, P. Chen, and S. S. Lau, Appl. Phys. Lett., 87, 091902 (2005)

[13] L. Shao, Y. Lin, J. G. Swadener, J. K. Lee, Q. X. Jia. Y. Q. Wang, M. Nastasi, P. E. Thompson, N. D. Theodore, T. L. Alford, J. W. Mayer, P. Chen, and S. S. Lau, Appl. Phys. Lett., 87, 251907 (2005)

[14] L. Shao, Y. Lin, J. G. Swadener, J. K. Lee, Q. X. Jia. Y. Q. Wang, M. Nastasi, P. E. Thompson, N. D. Theodore, T. L. Alford, J. W. Mayer, P. Chen, and S. S. Lau, Appl. Phys. Lett., 88, 021901 (2006)

[15] L. Shao, J. K. Lee, Y. Q. Wang, M. Nastasi, P. E. Thompson, N. D. Theodore, T. L. Alford, J. W. Mayer, P. Chen, and S. S. Lau, J. Appl. Phys., 99, 126105 (2006)

[16] G. D. Watkins, in *Handbook of Semiconductor Technology*, edited by K. A. Jackson, and W. Schröter (Wiley-VCH, Weinheim, 2000, Vol. 1, p. 135)

[17] S. Personic, A. Tauzin, K. K. Bourdelle, F. Letertre, N. Kernevez, F. Laugier, N. Cherkashin, A. Claverie, and R. Fortunier, 16th Int. Conf. on Ion Implantation Technology, AIP Conf. Proc., 866, 65 (2006)

[18] S. personnic, K. K. Bourdelle, F. Letertre, A. Tauzin, N. Cherkashin, and A. Claverie, J. Appl. Phys., 103, 023508 (2008)

[19] M. K. Weldon, V. E. Marsico, Y. J. Chabal, A. Agarwal, D. J. Eaglesham, J. Sapjeta, W. L. Brown, D. C. Jacobson, Y. Caudano, S. B. Christman, and E. E. Chaban, J. Vac. Sci. Technol. B 15, 1065 (1997)

[20] G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, Appl. Phys. Lett. 56, 656 (1990)

[21] M. K. Weldon, V. E. Marsico, Y. J. Chabal, D. R. Hamann, S. B. Christman, and E. E. Chaban, Surf. Sci. 368, 163 (1996)

[22] B. Bech Nielsen, L. Hoffmann, and M. Budde, Mater. Sci. Eng. B 36, 259 (1996)

[23] N. H. Nickel, G. B. Anderson, N. M. Johnson, and J. Walker, Phys. Rev. B, 62, 8012 (2000)

[24] N. M. p Johnson, F. A. Ponce, R. A. Street, and R. J. Nemanich, Phys. Rev. B, 35, 4166 (1987)

[25] M. Nastasi, T. Hochbauer, J-K. Lee, A. Misra, J.P. Hirth, M. Ridgway, T. Lafford, Appl Phys. Lett. 86, iss.15, 154102 (2005)

[26] L. Shao, Y. Lin, J. G. Swadener, J. K. Lee, Q. X. Jia, Y. Q. Wang, M. Nastasi, P. E. Thompson, N. D. Theodore, T. L. Alford, J. W. Mayer, P. Chen, and S. S. Lau, Appl. Phys. Lett., 88, 021901 (2006)

[27] E. V. Lavrov, J. Weber, L. Huang, B. Bech Nielsen, Phys. Rev. B, 64, 035204 (2001)

[28] S.-Y. Chung, N. Jin, A. T. Rice, P. R. Berger, Ronghua Yu, Z. Q. Fang, and P. E. Thompson, J. Appl. Phys. 93, 9104 (2003)

[29] S. -Y. Chung, N. Jin, R. E. Pavlovicz, P. R. Berger, Ronghua Yu, Z. Q. Fang, and P. E. Thompson, J. Appl. Phys., 96, 747 (2004)

[30] O. Moutanabbir, A. Giguère, and B. Terreault, Appl. Phys. Lett., 26, 3286 (2004)

[31] X. Lu, N. W. Cheung, M. D. Strathman, P. K. Chu, and B. Doyle, Appl. Phys. Lett., 71, 1804 (1997)

Table Captions

Table 1 Summary of SEM observations of the Si/$Si_{0.80}Ge_{0.20}$/Si samples after hydrogenation for various durations at 250 °C and 300 °C.

T (°C)	Time (h)	Blister Diameter (nm)	Blister Density (cm^{-2})
250	0.5	*	*
	1.0	*	*
	1.5	*	*
	2.0	7.7×10^{2}	3.1×10^{7}
300	0.5	3.0×10^{1}	8.8×10^{8}
	1.0	6.7×10^{2}	1.4×10^{7}
	1.5	1.3×10^{3}	8.8×10^{6}
	2.0	3.7×10^{3}**	2.0×10^{6}

*Blisters cannot be observed by SEM

**Exfoliated blisters (exfoliation has occurred)

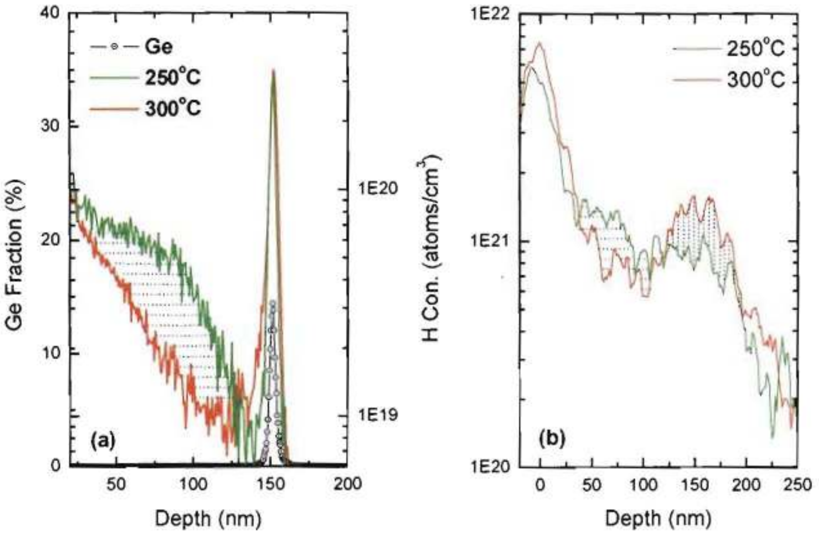
Table 1

Figure Captions

Fig. 1 (a)SIMS depth distribution of H and Ge atoms of Si/ $Si_{0.80}Ge_{0.20}$/Si heterostructure after 1 h plasma hydrogenation at 250 °C and 300 °C, and (b) ERD spectra of the Si/ $Si_{0.80}Ge_{0.20}$/Si heterostructure after 1 h plasma hydrogenation at 250 °C and 300 °C.

Fig. 2 MIR-IR spectra from the Si/$Si_{0.80}Ge_{0.20}$/Si heterostructure after 1 h plasma hydrogenation at 250 °C and 300 °C.

Fig. 3 The changes of MIR-IR spectra from as-hydrogenated Si/ $Si_{0.80}Ge_{0.20}$/Si heterostructure (1 h at 250 °C) to annealed heterostructures(4 h at 300 °C and 400 °C, respectively).



(a)
Ge
250°C
300°C
Ge Fraction (%)
0
10
20
30
40
1E19
1E20
50
100
150
200
Depth (nm)
(b)
250°C
300°C
H Con. (atoms/cm^3)
1E20
1E21
1E22
0
50
100
150
200
250
Depth (nm)

Fig. 1

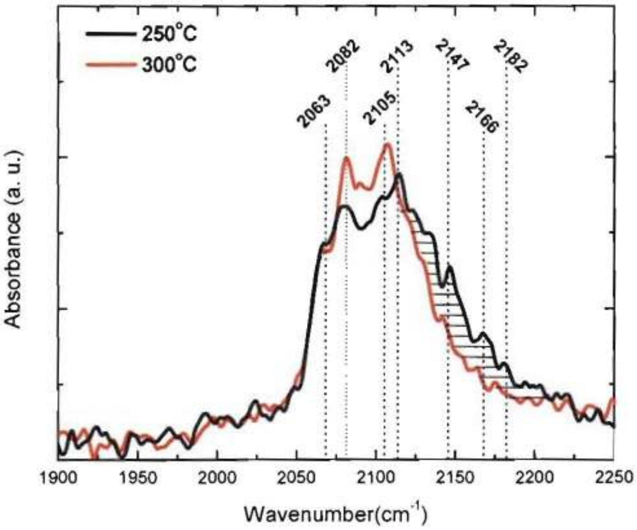

250°C
300°C
2063
2082
2105
2113
2147
2166
2182
Absorbance (a. u.)
1900
1950
2000
2050
2100
2150
2200
2250
Wavenumber(cm^{-1})

Fig. 2

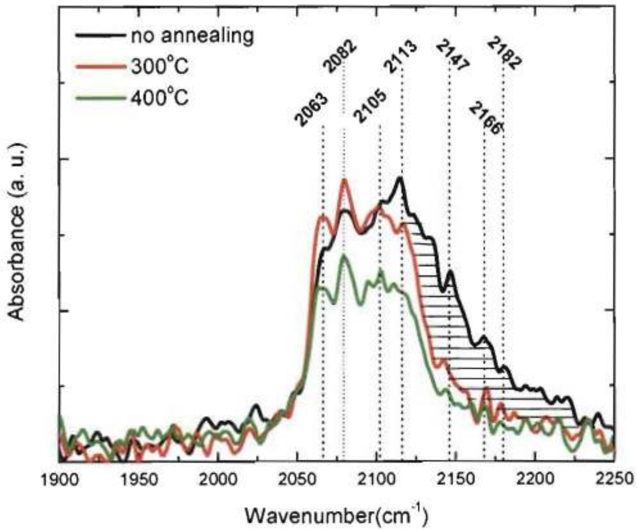

no annealing
300°C
400°C
2063
2082
2105
2113
2147
2166
2182
Absorbance (a. u.)
1900
1950
2000
2050
2100
2150
2200
2250
Wavenumber(cm^{-1})

Fig. 3