

# **Influence of Filament and Substrate Temperatures on Structural and Optoelectronic Properties of Narrow Gap a-SiGe:H Alloys Deposited by Hot-Wire CVD**

## **Preprint**

Y. Xu, B.P. Nelson, L.M. Gedvilas, and R.C. Reedy

*National Renewable Energy Laboratory*

D.L. Williamson

*Colorado School of Mines*

*To be presented at the 2003 Materials Research Society Spring Meeting  
San Francisco, California  
21-25 April 2003*



**National Renewable Energy Laboratory**

1617 Cole Boulevard  
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory  
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

## NOTICE

The submitted manuscript has been offered by an employee of the Midwest Research Institute (MRI), a contractor of the US Government under Contract No. DE-AC36-99GO10337. Accordingly, the US Government and MRI retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy  
and its contractors, in paper, from:

U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
phone: 865.576.8401  
fax: 865.576.5728  
email: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

Available for sale to the public, in paper, from:

U.S. Department of Commerce  
National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
phone: 800.553.6847  
fax: 703.605.6900  
email: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov)  
online ordering: <http://www.ntis.gov/ordering.htm>



# Influence of Filament and Substrate Temperatures on Structural and Optoelectronic Properties of Narrow Gap a-SiGe:H Alloys Deposited by Hot-Wire CVD

Yueqin Xu, Brent P. Nelson, D.L. Williamson\*, Lynn M. Gedvilas, and Robert C. Reedy

National Renewable Energy Laboratory  
1617 Cole Blvd., Golden CO 80401, USA

\*Colorado School of Mines, Department of Physics  
Golden, CO 80401, U.S.A.

## ABSTRACT

We have found that narrow-bandgap— $1.25 < E_{\text{Tauc Gap}} < 1.50$  eV—amorphous silicon germanium (a-SiGe:H) alloys grown by hot-wire chemical vapor deposition (hot-wire CVD) can be improved by lowering both substrate and filament temperatures. We systematically study films deposited using a one-tungsten filament, decreasing filament temperature ( $T_f$ ) from our standard temperature of 2150° down to 1750°C, and fixing all other deposition parameters. By decreasing  $T_f$  at the fixed substrate temperature ( $T_s$ ) of 180°C, the Ge-H bonding increases, whereas the Si-H<sub>2</sub> bonding is eliminated. Films with higher Ge-H bonding and less Si-H<sub>2</sub> have improved photoconductivity. For the series of films deposited using the same germane gas fraction at 35%, the energy where the optical absorption is  $1 \times 10^4$  (E04) drops from 1.54 to 1.41 eV with decreasing  $T_f$ . This is mainly due to the combination of an increasing Ge solid fraction ( $x$ ) in the film, and an improved homogeneity and compactness due to significant reduction of microvoids, which was confirmed by small angle X-ray scattering (SAXS). We also studied a series of films grown by decreasing the  $T_s$  from our previous standard temperature of 350°C down to 125°C, fixing all other deposition parameters including  $T_f$  at 1800°C. By decreasing  $T_s$ , both the total hydrogen content ( $C_H$ ) and the Ge-H bonding increased, but the Si-H<sub>2</sub> bonding is not measurable in the  $T_s$  range of 180°-300°C. The E04 increases from 1.40 to 1.51 eV as  $T_s$  decreased from 350° to 125°C, mainly due to the increased total hydrogen content ( $C_H$ ). At the same time, the photo-to-dark conductivity ratio increases almost three orders of magnitude over this range of  $T_s$ .

## INTRODUCTION

We first reported at the 1998 MRS Spring Conference that we can deposit high-quality a-SiGe:H alloys with bandgaps over 1.5 eV at high deposition rates over 10 Å/s by hot-wire CVD[1]. We then fabricated a-Si:H/a-SiGe:H tandem solar cells using these mid-gap a-SiGe:H alloys and obtained a conversion efficiency over 11% [2]. In the earlier papers, we showed that substrate temperatures over 270°C produced high-quality mid-gap materials. However for a-SiGe:H alloys below 1.5 eV (which we call narrow gap), we observed that high  $T_s$  and high  $T_f$  were deleterious to the film quality. Therefore, recently we focused our research on this narrow-bandgap region,  $1.25 \text{ eV} < E_{\text{Tauc Gap}} (E_{\text{Tauc}}) < 1.50 \text{ eV}$ , in different process regimes than used for our mid-gap materials [3, 4]. In this paper, we present the effect of  $T_f$  and  $T_s$  on the structural and optoelectronic properties of a-SiGe:H films grown by hot-wire CVD.

## EXPERIMENTAL DETAILS

We deposited two sets of films. The first set was deposited by reducing  $T_f$  from 2150°C to 1750°C with all other deposition parameters were fixed. The second set was deposited by reducing  $T_s$  from 350°C to 125°C with all other deposition parameters fixed. See Table 1 for a list of select deposition parameters, the film thicknesses and deposition rates (D.R.) for the films examined in this paper.

Table 1. Deposition Parameters of the Samples\*.

Sample (Set 1)	$T_f$ (°C)	$T_s$ (start) (°C)	Thick. (Å)	D. R. (Å/s)	Sample (Set 2)	$T_s$ (°C)	$T_f$ (start) (°C)	Thick. (Å)	D. R. (Å/s)
L902	2150	180	2976	9.92	L908	350	1800	2919	3.04
L904	2065	180	3434	8.18	L894	300	1800	4087	3.45
L905	1975	180	3315	6.50	L895	250	1800	3669	3.08
L907	1880	180	2997	4.16	L896	200	1800	3622	2.92
L911	1800	180	2128	2.03	L897	150	1800	3501	2.84
L913	1750	180	2085	0.98	L898	125	1800	2856	2.14

\* All samples are deposited using the same  $\text{GeH}_4$  gas ratio of  $\text{GeH}_4 / (\text{GeH}_4 + \text{SiH}_4) = 35\%$ , the same  $\text{H}_2$  dilution ratio of  $\text{H}_2 / (\text{GeH}_4 + \text{SiH}_4) = 1$ , and at the same deposition pressure of 15 mTorr.

The hot wire deposition chamber used in this study is a 10-cm-diameter  $\times$  30-cm-long stainless steel tube mounted inside of a standard high-vacuum 6-way cross [3]. The outside of this tube is wrapped with an encapsulated resistive heater in a pattern that provides an isothermal region in the center of the tube, the location of the substrate during deposition. The filament used in this study is one tungsten wire 0.38 mm in diameter and about 22 cm in straight length and 18 cm in coiled length. The spacing from the filament to substrate is 5 cm, and the  $T_f$  is calculated from tables listing the filament diameter and current, and is also calibrated by a two-wavelength pyrometer under vacuum conditions.

We deposited a-SiGe:H films simultaneously on 1737F Corning glass and c-Si wafers. We evaporated coplanar (width to length = 0.05) Cr contacts on the films on the 1737F substrates for conductivity measurements. We also performed optical measurements using an n&k 1280 analyzer on the films grown on 1737F substrates to determine the thickness (Å), bandgap ( $E_0$ ), which is the photon energy where the optical absorption is  $1 \times 10^4$ . The Tauc bandgap is taken from the fitting of  $E$  vs.  $(\alpha h\nu)^{1/2}$ , in which  $\alpha$  is calculated by the method of interference-free determination of optical absorption coefficient [5] on the raw transmission and reflectance data.

The FTIR absorption spectra were obtained from the films deposited on c-Si wafers by a Nicolet 510 system between 400 and 4000  $\text{cm}^{-1}$ . The hydrogen content of these films was determined by calculating the integrated absorption of local vibration wagging modes of Si-H, Ge-H mono-hydrogen bonds at the peak positions of about 640  $\text{cm}^{-1}$  and 570  $\text{cm}^{-1}$ , respectively [6, 7, 8].

For SAXS measurement, a duplicate set of films was deposited on high-purity aluminum-foil with conditions similar to those in Table 1. The total integrated SAXS intensity,  $Q_T$ , is a good measure of the overall film heterogeneity. The SAXS technique and analysis methods are described elsewhere [11]. The SIMS measurement was also taken on the films deposited on c-Si substrate by using a Cameca IMS-5F instrument to determinate the Ge solid-phase fraction ( $x$ ) in the films [12].

## RESULTS AND DISCUSSION

Between wavenumbers 1700 and 2100  $\text{cm}^{-1}$  on each set of FTIR spectra, there are stretch modes of mono-hydrogen bonds of Si-H and Ge-H corresponding to the peaks at approximately 2000 and 1880  $\text{cm}^{-1}$ , respectively, and di-hydrogen bonds of Si-H<sub>2</sub> and Ge-H<sub>2</sub> corresponding to the peaks at 2090 and 1980  $\text{cm}^{-1}$ , respectively. Superpositions of Gaussians were used to fit these peaks. Figures 1-a and 1-b show these peak fittings for the two sets of films in their stretch band regions. We found no evidence that polyhydrides of germanium were incorporated in these films; otherwise there would be additional peaks at 830 and 760  $\text{cm}^{-1}$  corresponding to the bending modes of polyhydrides of germanium ( $\text{GeH}_2$ )<sub>n</sub> [9, 10], analogous to the two peaks at 890 and 845  $\text{cm}^{-1}$ , which are a scissors mode corresponding to the bending modes of polyhydrides of silicon ( $\text{SiH}_2$ )<sub>n</sub>. Table 2 lists the results of the various measurements made on these samples listed in Table 1.

### The effects of varying filament temperature

Figure 2 shows that the deposition rate (D. R.), E04, and hydrogen content ( $C_H$ ) all monotonically decreased as  $T_f$  decreased from 2150° to 1750°C. The  $C_H$  in the films is relatively constant for this set (12-15 at.%) due to the fixed  $T_s$ , but a sharp decrease of D.R. can be seen from about 10 Å/s to 1 Å/s. This demonstrates that the D.R. is mainly dependent on the filament energy under the same deposition pressure. E04 also decreased from 1.54 to 1.41 eV with decrease of  $T_f$ . We observed that higher  $T_f$  resulted in higher deposition rates but due to the fixed low  $T_s$  at 180°C, the films are porous due to higher fraction of microvoids that usually coexist with polyhydrides of silicon- ( $\text{SiH}_2$ )<sub>n</sub>. As can be seen, when  $T_f$  is above 1900°C, there is a significant amount (~20% of  $C_H$ ) of Si-H<sub>2</sub> in the film (Fig. 3), but below 1900°C, the films improved rapidly as demonstrated by the decrease in Si-H<sub>2</sub> and increase in photoconductivity (Fig. 3). The relative amount of Ge-H bonding (to total H-bonding) increases monotonically with decreasing  $T_f$  (Fig. 3). This is an additional reflection of the improvement in film quality with decreasing  $T_f$  as Ge-H bonding

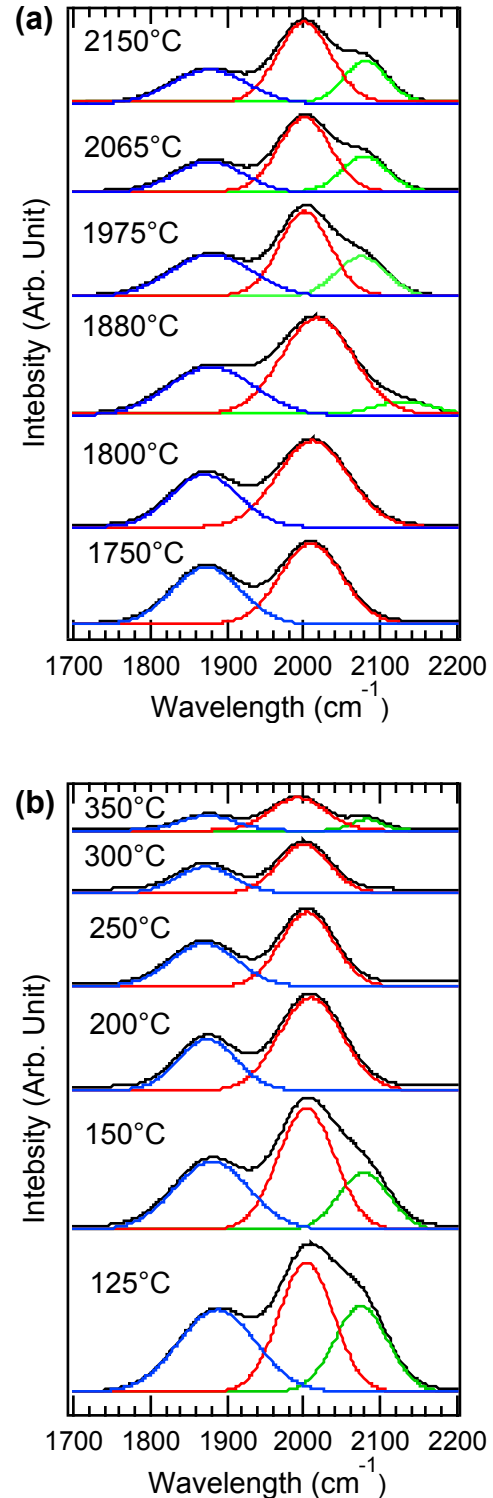


Fig. 1 Three-Gaussians fit to Si-H, Ge-H, and Si-H<sub>2</sub> bonding on the samples deposited under varying  $T_f$  (Fig. 1-a) and  $T_s$  (Fig. 1-b).

reflects favorable hydrogen passivation of Ge dangling bonds.

Table 2. Results of the Various Measurements Made on Samples Listed in Table 1.

Sample (Set 1&2)	$\sigma_{\text{photo}}$ ( $\text{cm}^{-1} \cdot \Omega^{-1}$ )	Ratio $\tilde{\sigma}_{\text{photo}}/\sigma_{\text{dark}}$	E04 (eV)	$E_{\text{Tauc}}$ (eV)	n ( $633\text{nm}^{-1}$ )	x (%)	$Q_{\text{T}}$ ( $10^{24}$ eu/ $\text{cm}^3$ )
L902	2.39e-07	356	1.54	1.33	4.511	57.4	20.1
L904	2.80e-07	800	1.54	1.33	4.504	57.4	18.3
L905	3.56e-07	983	1.53	1.32	4.512	60.5	9.92
L907	7.51e-07	736	1.50	1.30	4.685	NA	7.24
L911	6.11e-06	382	1.45	1.26	4.783	66.3	2.61
L913	5.11e-06	203	1.41	1.21	5.054	70.3	1.89
L908	3.53e-07	1	1.40	1.21	4.833	59.7	9.91
L894	8.93e-07	48	1.43	1.23	4.875	61.3	4.58
L895	1.95e-06	179	1.45	1.26	4.875	63.4	2.18
L896	2.10e-06	346	1.47	1.28	4.985	64.6	2.72
L897	8.25e-07	292	1.49	1.29	4.691	64.5	7.11
L898	9.65e-07	283	1.50	1.31	4.711	68.7	10.7

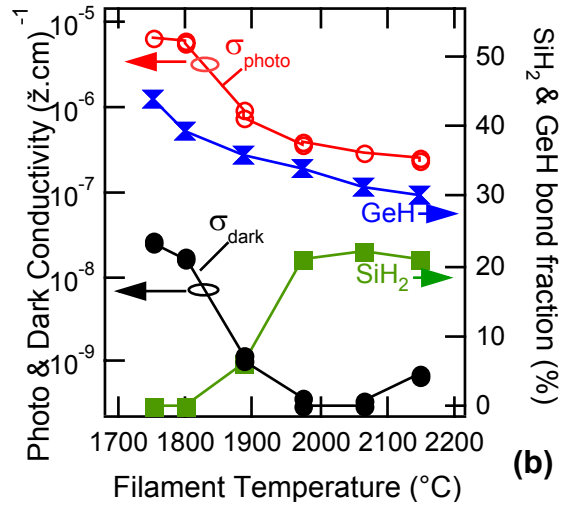
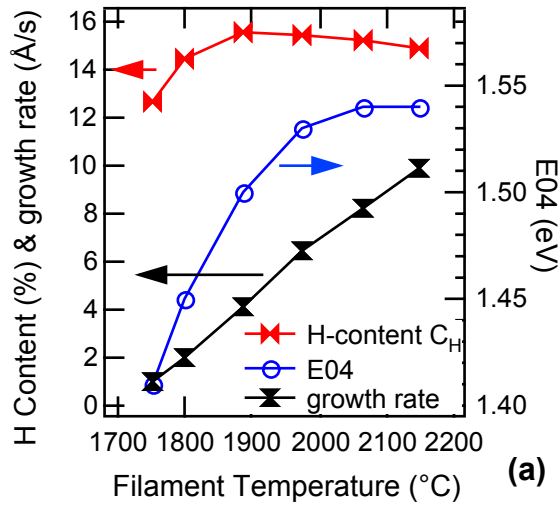


Fig. 2. Variation of deposition rate, E04, and hydrogen content as a function of  $T_f$ .

Fig. 3. The effects of  $T_f$  on  $\sigma_{\text{photo}}$ ,  $\sigma_{\text{dark}}$ , and Ge-H, Si-H<sub>2</sub> bonding fractions.

The total integrated SAXS intensity decreases monotonically with decreasing  $T_f$ , whereas the Ge solid-phase fraction  $x$  increases (Fig. 4). This inverse correlation is somewhat surprising, yet may be explained by the fact that the films with higher Ge are grown at lower deposition rates, and thus have improved microstructure.

The higher Ge at lower  $T_f$  is due to the lower dissociation energy for  $\text{GeH}_4$  relative to  $\text{SiH}_4$ . The decrease in E04 with decreasing  $T_f$  (Fig. 2), is due primarily to the increase in Ge solid phase fraction (Fig. 4), but also to improved film homogeneity and compactness due to significant reduction of microvoids indicated by the SAXS measurements (Fig. 4).

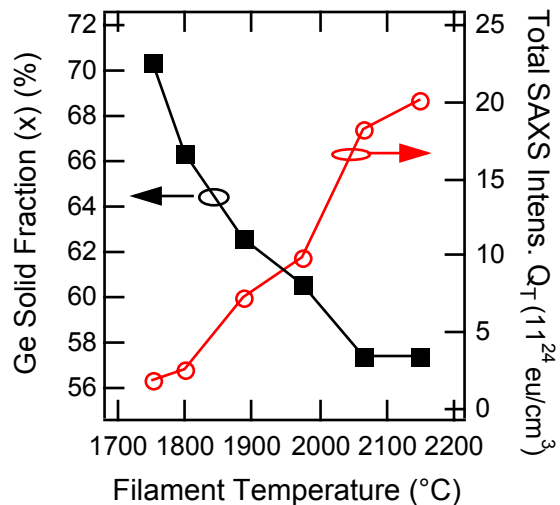


Fig. 4. Increase of Ge fraction  $x$  and decrease of total SAXS intensity  $Q_T$  with decrease of  $T_f$ .

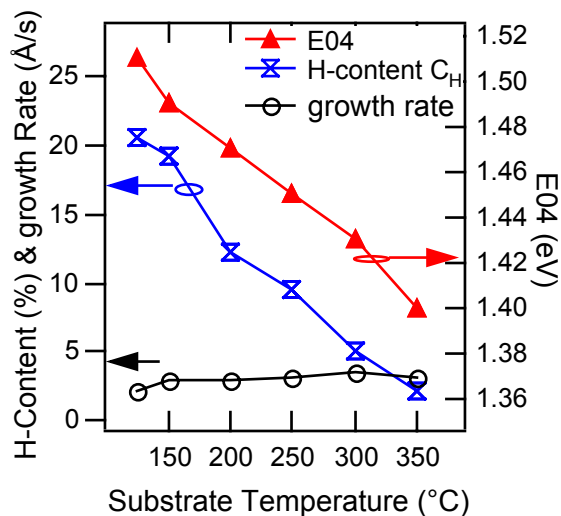


Fig. 5. Variation of deposition rate, E04, and hydrogen content as a function of  $T_f$ .

### The effects of varying substrate temperature

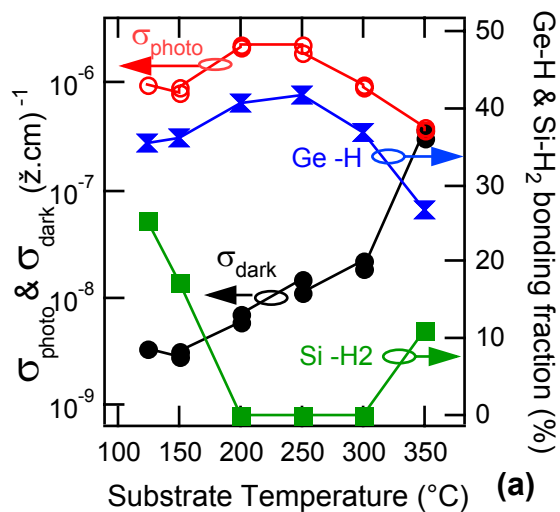


Fig. 6. The effects of  $T_s$  on  $\sigma_{\text{photo}}$ ,  $\sigma_{\text{dark}}$ , and Ge-H, Si-H<sub>2</sub> bonding fractions.

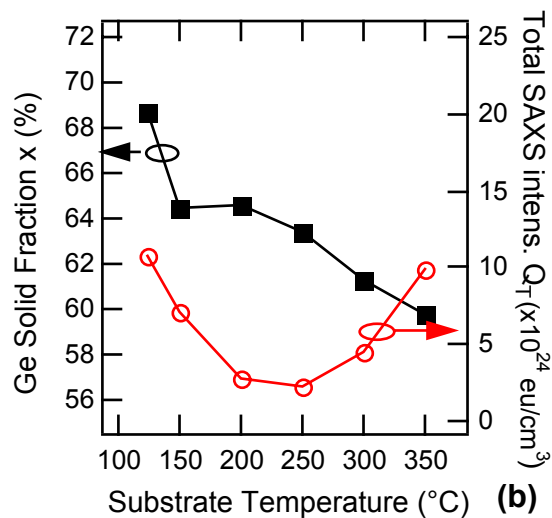


Fig. 7. Smaller increase of Ge fraction  $x$  and decrease of total SAXS intensity  $Q_T$  at the  $T_s$  of 200°-250°C.

In Fig 5, we show that both E04 and  $C_H$  are dependent on  $T_s$ , whereas the growth rate is not strongly affected by  $T_s$ , remaining  $\sim 2\text{-}4$  Å/s. When  $T_s$  is between 200°- 300°C, Si-H<sub>2</sub> is below the detection limit of FTIR, which is accompanied by increased photoconductivity (Fig. 6).

The total hydrogen  $C_H$  in the films increases monotonically from  $\sim 2\%$  to  $\sim 20\%$  as the  $T_s$  is lowered from 350° to 125°C. This large change in  $C_H$  has a strong influence on E04, which increases from 1.4 to 1.5 eV with the same decrease of  $T_s$ . The relative amount of Ge-H bonding is a maximum in the optimized temperature range of 200°- 300°C, which correlates nicely with

higher photoconductivity (Fig. 6). The lowering of  $T_s$  has a profound improvement (lowering) of the dark conductivity (Fig. 6).

The total integrated SAXS intensity is a minimum in the optimized temperature range of 200°- 300°C, whereas Ge increases monotonically with decreasing  $T_f$  (Fig. 7). The improvement of optoelectronic properties in this optimized  $T_s$  range correlates nicely with the SAXS intensity, even though there is a small increase of Ge fraction  $x$  (Fig. 7).

## CONCLUSIONS

Based on above evidence, lowering  $T_f$  (<1850°C) and optimizing  $T_s$  (200°-250°C) can improve the structural and optoelectronic properties of narrow-gap a-SiGe:H alloys deposited by HWCVD, in which a 0.38-mm tungsten wire was used, resulting in a D.R. of about 3Å/s. The improved material has about 65% Ge, an optical band gap around 1.3 eV, and an activation energy about 0.64 eV. This material has a  $C_H$  of about 10%, with over 40% of Ge-H bonding and about 60% of Si-H bonding but without detectable di-hydride bonding (Si-H<sub>2</sub>, Ge-H<sub>2</sub>). Therefore, this material has higher photoconductivity ( $\sim 10^{-6}$ ) and photosensitivity (about 200-500). This material has much improved homogeneity as measured by SAXS, compared to all other such alloys with high Ge content.

## ACKNOWLEDGMENT

This work was performed under DOE contract number DE-AC36-99GO10337.

## REFERENCES

1. B.P. Nelson, Y. Xu, D.L. Williamson, B. von Roedern, A. Mason, S. Heck, A.H. Mahan, S.E. Schmitt, A.C. Gallagher, J. Webb, and R. Reedy, *Mat. Res. Soc. Symp. Proc.* 507 (1998) 447.
2. Q. Wang, E. Iwaniczco, J. Yang, K. Lord, and S. Guha, *Mat. Res. Soc. Symp. Proc.* 664 (2001) A7.5.
3. Y. Xu, B.P. Nelson, L.M. Gedvilas, and R.C. Reedy, Sept. 2002, 2<sup>nd</sup> Intern. Conf. on Cat-CVD (Hot-Wire CVD) Process, Denver, Colorado, *Thin Solid Films* (in press).
4. B.P. Nelson, Y. Xu, D.L. Williamson, D. Han, R. Braunstein, M. Boshta, and B. Alavi, Sept. 2002, 2<sup>nd</sup> Intern. Conf. on Cat-CVD Process, Denver, Colorado, *Thin Solid Films* (in press).
5. Yoshihilo Hishkawa, NoBoru Nakamura, Shinya Tsuda, Shoichi Nakano, Yasuo Kishi, and Yukinori Kuwano, *Jpn. J. Appl. Phys.* 30 (1991) 1008.
6. C.J. Fang, K.J. Gruntz, L. Ley, M. Cardona, F.J. Demond, G. Muller, S. Kalbitzer, *J. Non-Cryst. Solids* 35 & 36 (1980) 255.
7. M. Cardona, *Phys. Stat. Sol. (b)* 118 (1983) 463.
8. A.A. Langford, M.L. Fleet, B.P. Nelson, W.A. Lanford, N. Maley, *Phys. Rev.* B45 (1992) 13367.
9. Mohan Krishan Bhan, L.K. Malhotra, and Subhash C. Kashyap, *J. Appl. Phys.* 66 (1989) 2528.
10. G. Lucovsky, *J. Non-Cryst. Solids* 76 (1985) 173.
11. D.L. Williamson, *Mat. Res. Soc. Symp. Proc.* 377 (1995) 251.
12. R.C. Reedy, A.R. Mason, B.P. Nelson, Y. Xu, American Institute of Physics, NICH Report No. 27431 (1999) pp. 537-541.



REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE April 2003	3. REPORT TYPE AND DATES COVERED Conference Paper		
4. TITLE AND SUBTITLE Influence of Filament and Substrate Temperatures on Structural and Optoelectronic Properties of Narrow Gap a-SiGe:H Alloys Deposited by Hot-Wire CVD: Preprint			5. FUNDING NUMBERS PVP34101	
6. AUTHOR(S) Y. Xu, B.P. Nelson, L.M. Gedvilas, R.C. Reedy, and D.L. Williamson*				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401-3393 *Colorado School of Mines, Department of Physics, Golden, CO 80401			8. PERFORMING ORGANIZATION REPORT NUMBER NREL/CP-520-33936	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161			12b. DISTRIBUTION CODE	
13. ABSTRACT ( <i>Maximum 200 words</i> ): We have found that narrow-bandgap— $1.25 < T_{\text{auc Gap}} < 1.50$ eV—amorphous silicon germanium (a-SiGe:H) alloys grown by hot-wire chemical vapor deposition (CVD) can be improved by lowering both substrate and filament temperatures. We systematically studied films deposited using a one-tungsten filament, decreasing filament temperature ( $T_f$ ) from our standard temperature of 2150° down to 1750°C, and fixing all other deposition parameters. By decreasing $T_f$ at the fixed substrate temperature ( $T_s$ ) of 180°C, the Ge-H bonding increases, whereas the Si-H <sub>2</sub> bonding is eliminated. Films with higher Ge-H bonding and less Si-H <sub>2</sub> have improved photoconductivity. For the series of films deposited using the same germane gas fraction at 35%, the energy where the optical absorption is $1 \times 10^4$ (E04) drops from 1.54 to 1.41 eV with decreasing $T_f$ . This is mainly due to the combination of an increasing Ge solid fraction (x) in the film, and an improved homogeneity and compactness due to significant reduction of microvoids, which was confirmed by small-angle X-ray scattering (SAXS). We also studied a series of films grown by decreasing the $T_s$ from our previous standard temperature of 350°C down to 125°C, fixing all other deposition parameters including $T_f$ at 1800°C. By decreasing $T_s$ , both the total hydrogen content and the Ge-H bonding increased, but the Si-H <sub>2</sub> bonding is not measurable in the $T_s$ range of 180°-300°C. The E04 increases from 1.40 to 1.51 eV as $T_s$ decreased from 350° to 125°C, mainly due to the increased total hydrogen content. At the same time, the photo-to-dark conductivity ratio increases almost three orders of magnitude over this range of $T_s$ .				
14. SUBJECT TERMS: PV; amorphous silicon germanium; hot-wire chemical vapor deposition; narrow bandgap; tandem solar cells; X-ray scattering (SAXS); photoconductivity; photosensitivity; optoelectronic;			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	