Ga configurations in hydrogenated amorphous silicon as studied by x-ray photoemission spectroscopy

Z. H. Lu,* S. Poulin-Dandurand, E. Sacher, and A. Yelon
Groupe des Couches Minces et Département de Génie Physique, École Polytechnique de Montréal, Case Postale 6079, Succursale A, Montréal, Québec, Canada H3C 3A7
(Received 5 March 1990)

Samples of crystalline silicon and glow-discharge-deposited hydrogenated amorphous silicon were doped with gallium by low-energy (4-keV) ion implantation. X-ray photoemission spectroscopy was used to study the chemical-bonding states of the Ga. From Ga 3*d* core-level studies, we found that elementary interstitial, threefold-coordinated, and fourfold-coordinated Ga coexist in the ion-implanted and annealed amorphous silicon network. The percentage of activated threefold- and fourfold-coordinated Ga atoms is found to increase with increasing annealing temperature, prior to crystallization. The energy released by the amorphous silicon lattice upon annealing contributes to the activation of the gallium from the elementary state to the threefold- or fourfold-coordinated state. No evidence of Ga—H bond formation is found. The percentage of fourfold-coordinated Ga, which we call the doping efficiency, ranges from 5% to 10%, depending upon the thermal treatment.

I. INTRODUCTION

The determination of the coordination structures of dopant atoms in hydrogenated amorphous silicon (*a*-Si:H) has been a subject of interest since the discovery made by Spear and LeComber[1] in 1975 that *a*-Si:H can be substitutionally doped *n* or *p* type by the addition of small amounts of phosphine or diborane to the silane plasma. It is now well established that the dopability of *a*-Si:H, in terms of detectable free carriers donated by the dopants, is attributed to the presence of hydrogen, which eliminates most of the localized density of states between the valence and conduction bands. However, the coordination structure of a dopant atom in *a*-Si, with or without the presence of hydrogen, is still poorly understood.

Since the tetrahedral sp^3 hybrid of Si is preserved in the material, a dopant (group-III or -V elements) that can donate an electron or a hole should also be in a fourfold-coordinated sp^3 hybrid.[2] That is, a fourfold-coordinated dopant will be capable of donating (group V) or accepting (group III) an electron.[2] Whether this yields a carrier or not will depend upon the density of trap states. Because of the possibility of a large variation in bond angle and bond length, the *a*-Si network also accommodates other bonding geometries, such as trigonal sp^2 or a nonbonding interstitial in the material.[2] Thus, in this paper, the doping efficiency will be defined as the fraction of dopant atoms which are fourfold coordinated. As just indicated, this may be considerably larger than the fraction which contributes carriers.

Several analytical techniques, such as extended x-ray-absorption fine structure[3] (EXAFS) and nuclear magnetic resonance[4] (NMR), have been used to determine dopant coordination structures in *a*-Si:H. In this paper, we used x-ray photoelectron spectroscopy (XPS) to study the coordination structures of Ga in *a*-Si:H.

II. EXPERIMENT

The doping of Ga was obtained by low-energy (4-keV) ion implantation and rapid thermal annealing (RTA). The details of these techniques are described elsewhere.[5] Both hydrogenated *a*-Si (*a*-Si:H) and initially crystalline (*c*-Si) samples were used for ion implantation. Thin *a*-Si:H films of about 1 μm in thickness were deposited by glow discharge (GD) onto *c*-Si substrates at 270 °C. The *c*-Si samples were *n* type and (100) oriented. Samples were implanted with about 15 at. % Ga close to the surface and were then annealed by RTA at various temperatures between 250 and 400 °C for 5 s. It has been shown that most of the hydrogen remains in *a*-Si:H after 5 s RTA at temperatures lower than 400 °C.[6] The *c*-Si was amorphous after Ga implantation. No indication of crystallization was found by low-energy electron diffraction (LEED) for both *c*-Si and *a*-Si:H samples. In order to avoid confusion, we will describe the Ga ion-implanted *c*-Si as *a*-Si (amorphous silicon) in what follows. The samples were etched in HF solution prior to being transferred for XPS measurements. We found that residual contamination after HF etching is limited to the topmost atomic layer.[7] This has a negligible effect on XPS measurements, which have a sampling depth of about 25 atomic layers.

The XPS measurements were carried out on a VG ESCALAB MK II system. Mg $K\alpha$ radiation (1253.6 eV) was used as the x-ray source. Both Si 2*p* and Ga 3*d* photoelectrons were recorded and then analyzed by a least-squares curve-fitting method. Since Si 2*p* presents a broad and invariant feature over the annealing temperature regime of 250–400 °C, only the Ga 3*d* spectra will be presented here.

III. RESULTS AND DISCUSSION

A. Determination of Ga coordinations from chemical-shift studies

In Fig. 1 we show Ga $3d$ core-level spectra recorded as as-implanted and -annealed a-Si samples. The input data for the Ga $3d$ doublet are a spin-orbit-splitting energy of 0.4 eV, an intensity ratio of $3d_{3/2}$ to $3d_{5/2}$ of 2:3, a full width at half maximum (FWHM) of the convolving function of 1.2 eV, and a Gaussian-to-Lorentzian mixing ratio of 0.6. The above parameters were found to be the best fit to the experimental data and were fixed for all Ga $3d$ core levels.

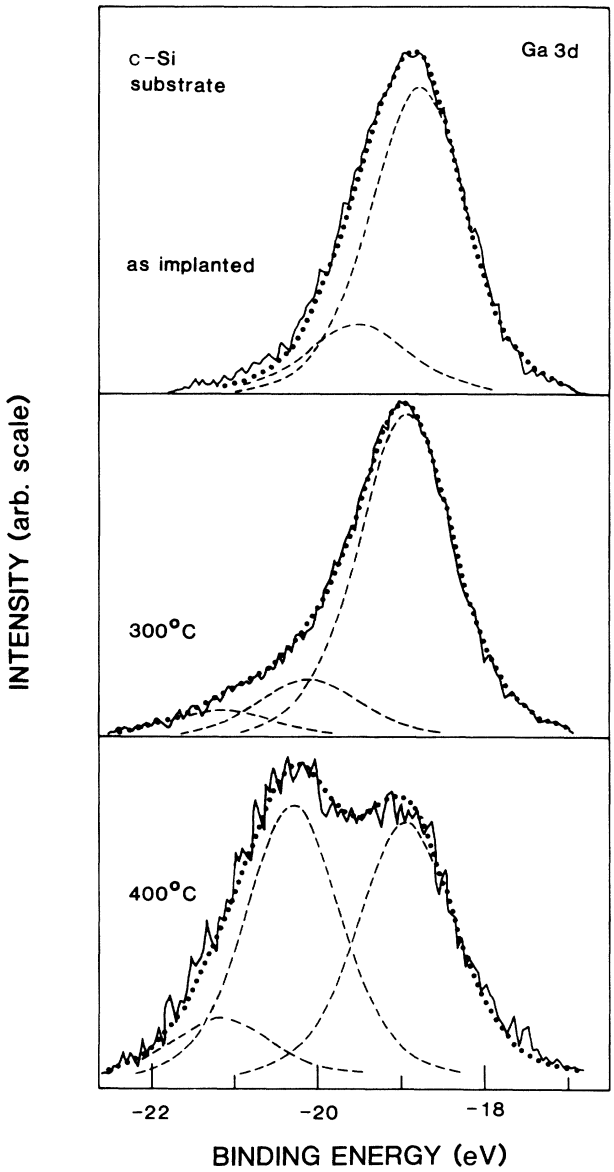

FIG. 1. Ga $3d$ core-level spectra measured on a-Si samples: as-implanted and -annealed at 300 and 400 °C. The experimental signals are shown by solid curves. The dashed curves show the results of curve resolution into different components, and the dots are the sums of the components. Intensities are shown on an arbitrary scale.

In Fig. 1 the resolved peaks are shown as dashed curves, which are the sums of the $3d_{3/2}$ and $3d_{5/2}$ spin-orbit doublets. The sums of these resolved peaks are shown as dotted curves. The experimental data are shown as solid lines. For the as-implanted sample, two peaks, at binding energies of 18.8 and 19.5 eV, were found to provide the best fit to the experimental data, as shown in the figure. For annealed samples, however, three peaks at binding energies of 18.8, 20.0, and 21.1 eV were resolved. The positions of each of these peaks were obtained from several samples, with a statistical error of 0.1 eV, and were confirmed by measuring the energy difference between the Si $2p_{3/2}$ and Ga $3d_{5/2}$ lines.

The peak at 18.8 eV corresponds to elementary gallium, $Ga_{(0)}$.[8] We assign the chemically shifted peaks at energies of 19.5, 20.0, and 21.1 eV to $Ga_{(2)}$, $Ga_{(3)}$, and $Ga_{(4)}$, which are twofold-, threefold-, and fourfold-coordinated gallium bonded to Si, respectively. The chemical shift to high binding energy in the coordinated Ga samples indicates that charges are transferred from gallium to silicon upon the formation of Ga—Si bonds. This is also consistent with the fact that Ga is less electronegative than Si, and consequently, charges will be transferred to Si upon the formation of Si—Ga bonds. The chemical shifts of $Ga_{(2)}$ and $Ga_{(3)}$ of 0.7 and 1.2 eV are in good agreement with synchrotron photoemission measurements of Ga on c-Si surfaces.[8]

The chemical shift per Si—Ga bond can be calculated by dividing the total chemical shift by the coordination number of the corresponding peak. This gives chemical shifts per Si—Ga bond of 0.35, 0.40, and 0.59 eV for $Ga_{(2)}$, $Ga_{(3)}$, and $Ga_{(4)}$, respectively. The large shift per Si—Ga bond for the $Ga_{(4)}$ state may be explained by its specific orbital properties. As a substitutional dopant in the Si matrix, the $Ga_{(4)}$ atom has to draw an extra electron from the Si matrix to form the tetrahedral sp^3-hybrid orbital state and create a hole in the Si matrix. The $Ga_{(3)}$ is a trigonal sp^2 hybrid in the amorphous-silicon continuous random network (CRN).[2] It is well known that the electronegativity depends strongly on the orbital hybrid state.[9] The attraction of an electron by an atom reduces its electronegativity (principle of electronegativity equalization[9]). This is all the more so when $Ga_{(3)}$ obtains an electron and rehybridizes to $Ga_{(4)}$. This means that $Ga_{(4)}$ will lose more electrons per bond to neighboring Si atoms, which remain sp^3 hybridized, than does $Ga_{(3)}$. Consequently, the largest chemical shift is expected for the tetrahedral Ga—Si bond.

The annealing-activated, threefold- and fourfold-coordinated Ga states are also observed with ion-implanted a-Si:H samples. In Fig. 2, we show the Ga $3d$ core-level spectra recorded on annealed a-Si:H. The three resolved peaks correspond to (from right to left) $Ga_{(0)}$, $Ga_{(3)}$, and $Ga_{(4)}$, respectively. The binding energies and chemical shifts of these peaks are the same as those observed with a-Si. This excludes the possibility that these peaks are related to Ga—H bonding states.

B. Activation of Ga and doping efficiency

In Table I, we give the fractions of differently coordinated Ga in Si, as well as the total Ga concentration

shown in Figs. 1 and 2. In Fig. 3, we show the logarithm of the fraction of threefold- or fourfold-coordinated gallium, $[Ga_{(3)}]/[Ga]$ and $[Ga_{(4)}]/[Ga]$, as a function of annealing temperature. These are obtained simply by dividing the intensities of the $Ga_{(3)}$ and $Ga_{(4)}$ peaks by the sum of the intensities of all the resolved peaks. From Table I and Fig. 3, we can see that the number of activated $Ga_{(3)}$ atoms is approximately twice that of $Ga_{(4)}$ atoms, in both a-Si:H and a-Si samples, in the temperature range 250–350 °C. The variation of $[Ga_{(i)}]$ $(i=3,4)$ with annealing temperature T_a may be fitted to the form

$$[Ga_{(i)}]/[Ga] \propto \exp(-E_a/kT_a) ,$$

where E_a is an activation energy. This yields an activation energy of 0.14 ± 0.05 eV for both threefold- and fourfold-coordinated Ga atoms.

TABLE I. Fractions of differently (i-fold-) coordinated gallium $[Ga_{(i)}]/[Ga]$ and total Ga concentrations c measured after annealing at various temperatures. Values in parentheses are for a-Si; other values are for a-Si:H.

	$[Ga_{(0)}]/[Ga]$			
T_a (°C)	250	300	350	400
$[Ga_{(0)}]/[Ga]$	0.85	0.82	0.77	
		(0.78)		(0.43)
$[Ga_{(3)}]/[Ga]$	0.10	0.13	0.15	
		(0.14)		(0.47)
$[Ga_{(4)}]/[Ga]$	0.05	0.05	0.08	
		(0.08)		(0.10)
c (at. %)[a]	15	12	6	
	(15)	(11)		(9)

[a]The Ga concentration was determined from Ga $3d_{5/2}$ and Si $2p_{3/2}$ core-level peak intensities with sensitivity factors of 0.31 and 0.25, respectively (Ref. 20).

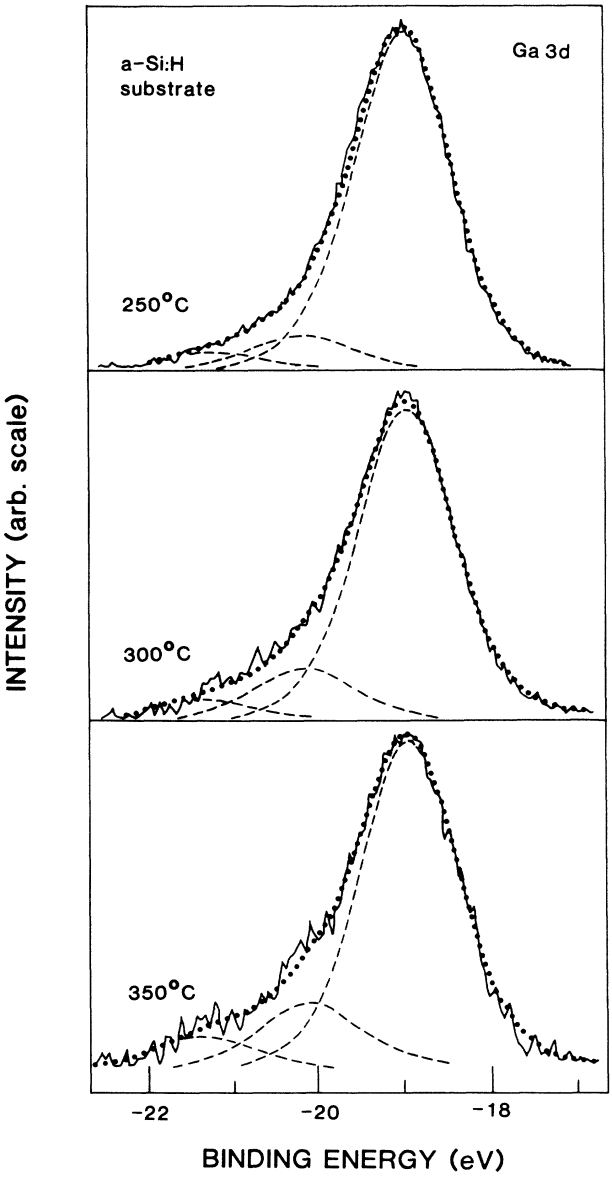

FIG. 2. Ga $3d$ core-level spectra measured on ion-implanted and annealed a-Si:H samples. The experimental signals are shown by solid lines. The dashed curves show the results of curve resolution into different components, and the dots are the sums of the components. Intensities are shown on an arbitrary scale.

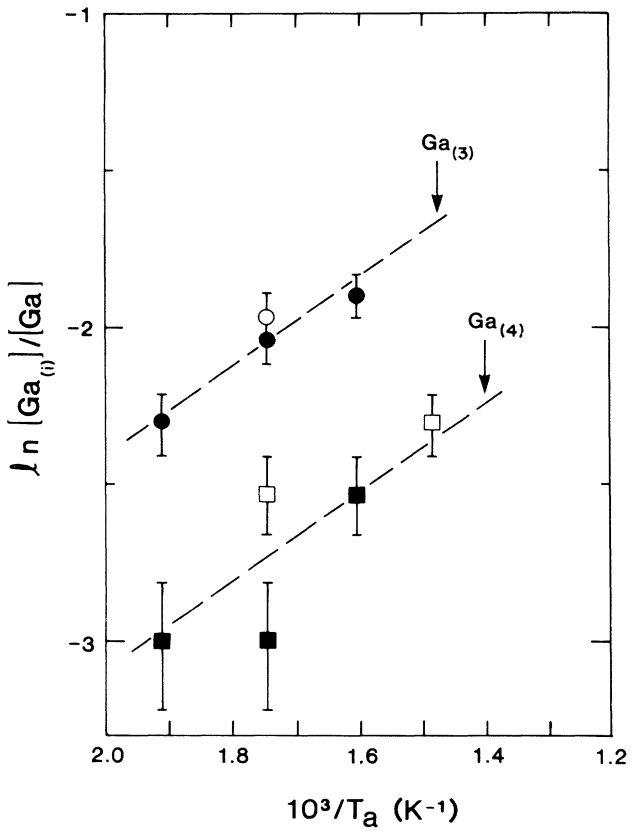

FIG. 3. Variations of the fractional concentrations, $[Ga_{(i)}]/[Ga]$ $(i=3,4)$, components as a function of annealing temperature T_a. Data were obtained on a-Si (solid circles and squares) and a-Si:H (open circles and squares).

From Raman scattering and neutron-diffraction studies, Fortner and Lannin[10,11] have found that Si and Ge lattices, which had been rendered amorphous by Ar^+-ion implantation, transformed to a more ordered structure by way of structural relaxation upon annealing. $\Delta\theta$, the mean Si—Si bond-angle variation or the width of the *a*-Si CRN bond-angle distribution function $P(\theta)$, was found to decrease about 2°,[10,11] for both Si and Ge upon annealing at 350 °C. The release of the elastic potential energy stored in the bond-angle deviations is brought about by structural relaxation or bond-angle ordering. This released energy was also detected in ion-implanted Ge (Ref. 12) and more recently in ion-implanted Si (Ref. 13) by differential-scanning-calorimetry experiments. Structural relaxation and lattice ordering prior to crystallization were also found in low-temperature-deposited and post-annealed *a*-Si and *a*-Ge.[14,15] From studies on the photoemission valence-band densities of states of our samples, we also found evidence of structural relaxation in Ga-ion-implanted *a*-Si and *a*-Si:H.[16]

The value of E_a for the activation of threefold- and fourfold-coordinated gallium is very close to an activation energy of 0.16 eV for H_{SR} reported by Fortner and Lannin.[10] H_{SR} is the amount of heat released upon structural relaxation, that is, the ordering in the *a*-Si and *a*-Ge CRN during an anneal of ion-implanted Si and Ge. This suggests that the activation of elementary Ga into threefold- or fourfold-coordinated bonding states occurs on structural relaxation of the silicon CRN. The similar activation behavior of $Ga_{(3)}$ and $Ga_{(4)}$ also suggests that the barriers between the elementary s^2p^1 to sp^2 and the $(s^2p^1+e^-)$ to sp^3 conversions might differ only slightly. The relatively high concentration of $Ga_{(3)}$ in the CRN could be explained by the fact the $Ga_{(3)}$ sp^2 orbital is generally lower in energy than the $Ga_{(4)}$ sp^3 hybrid, provided that the *a*-Si CRN is sufficiently flexible to accommodate this configuration.

One of the most important and controversial physical parameters in amorphous semiconductors is the solid-phase doping efficiency η_{sol}. This is defined as the number of donors or acceptors, which are presumably fourfold-coordinated dopants,[2] divided by the total dopant concentration,[17] that is, $[Ga_{(4)}]/[Ga]$ in our studies. The core-level spectral measurements shown in Table I indicate that η_{sol} varies from 5% to 10% for Ga concentrations ranging from 15 to 6 at. %. The decrease in Ga concentration upon annealing is due to the diffusion of Ga.

Various experimental techniques have been used to deduce the doping efficiency. EXAFS and NMR measurements on As and P in *a*-Si:H suggested that the concentration of fourfold-coordinated donors could be as high as 20% for samples with total concentration around 1 at. %.[3,4] This is believed to be overestimated.[17,18] Based on electrical measurements, Stutzmann[17] and Jousse *et al.*[19] showed that the solid-phase doping efficiency is less than 10% for various dopants over a wide range of doping levels. This is consistent with the present XPS measurements.

IV. CONCLUSIONS

In this paper, XPS has been used to measure the Ga chemical bonding states in amorphous silicon. Since XPS is a surface-sensitive analytical technique (with a sampling depth of about 50 Å), the doping of Ga was done by low-energy (4-keV) ion implantation. Both *c*-Si and GD *a*-Si:H samples were ion implanted with Ga. The *c*-Si was amorphous after the gallium-ion implantation and, therefore, represents the structural properties of unhydrogenated amorphous silicon (*a*-Si). From Ga 3*d* core-level studies, we found that Ga atoms are mostly in the elementary $Ga_{(0)}$ state, along with a small amount of gallium twofold bonded to Si. $Ga_{(2)}$ is an unstable state and disappears upon annealing. The $Ga_{(0)}$ is promoted to either a threefold- or fourfold-coordinated state after annealing. The percentage of $Ga_{(3)}$ and $Ga_{(4)}$ in *a*-Si CRN increases with increasing annealing temperatures prior to crystallization. We also found that the energy released by the silicon structural relaxation contributes to the activation of Ga from the elementary state to either the threefold- or fourfold-coordinated states. No evidence for Ga—H bonding has been found. The behavior of coordination structures in amorphous silicon is largely controlled by the properties of the silicon CRN.

ACKNOWLEDGMENTS

We wish to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada, the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche du Québec, and the Ministry of Energy, Mines and Resources of Canada.

*Present address: Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7.

[1]W. E. Spear and P. G. LeComber, Solid State Commun. **17**, 1193 (1975).

[2]J. Robertson, Phys. Rev. B **28**, 4647, 4658, and 4666 (1983).

[3]J. C. Knights, T. M. Hayes, and J. C. Kikkelsen, Jr., Phys. Rev. Lett. **39**, 712 (1977).

[4]J. A. Reimer and T. M. Duncan, Phys. Rev. B **27**, 4895 (1983).

[5]Z. H. Lu, E. Sacher, A. Selmani, and A. Yelon, Appl. Phys. Lett. **54**, 2665 (1989).

[6]P. Fiorini, I. Haller, J. J. Nocera, S. A. Cohen, and M. H. Brodsky, J. Appl. Phys. **62**, 1425 (1987).

[7]Z. H. Lu, E. Sacher, and A. Yelon, Philos. Mag. B **58**, 385 (1988).

[8]R. D. Bringan, M. A. Olmstead, R. I. G. Uhrberg, and R. Z. Bachrach, Phys. Rev. B **36**, 9569 (1987).

[9]D. Bergmann and J. Hinze, in *Electronegativity*, edited by K. D. Sen and C. K. Jørgensen (Springer-Verlag, New York, 1987), p. 145.

[10]J. Fortner and J. S. Lannin, Phys. Rev. B **37**, 10 154 (1988).

[11]J. Fortner and J. S. Lannin, Phys. Rev. B **39**, 5527 (1989).

[12]E. P. Donovan, F. Spaepen, D. Turnbull, J. M. Poate, and D.

C. Jacobson, J. Appl. Phys. **57**, 1795 (1984).
[13]S. Roorda, S. Doorn, W. C. Sinke, P. M. L. O. Scholte, and E. van Loenen, Phys. Rev. Lett. **62**, 1880 (1989).
[14]M. A. Paesler, D. E. Sayer, R. Tsu, and J. Gonzales-Hernandez, Phys. Rev. B **28**, 4550 (1983).
[15]R. Tsu, J. Gonzales-Hernandez, and F. H. Pollak, J. Non-Cryst. Solids **66**, 109 (1984).
[16]Z. H. Lu, E. Sacher, and A. Yelon (unpublished).
[17]M. Stutzmann, Philos. Mag. B **53**, L15 (1986).
[18]M. Stutzmann, D. K. Biegelson, and R. A. Street, Phys. Rev. B **35**, 5666 (1987).
[19]D. Jousse, J. C. Bruyère, E. Bustarret, and A. Deneuville, Philos. Mag. Lett. **55**, 41 (1987).
[20]D. Briggs and M. P. Seah, in *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy,* edited by D. Briggs and M. P. Seah (Wiley, New York, 1983), p. 511.