Solid-phase crystallization kinetics in doped *a*-Si chemical-vapor-deposition films

R. Bisaro and J. Magariño

Laboratoire Central de Recherches, Thomson-Compagnie Générale de Télégraphie Sans Fil, Boîte Postale 10, F-91401 Orsay, France

K. Zellama, S. Squelard, and P. Germain

Groupe de Physique des Solides de l'Ecole Normale Supérieure, Université de Paris VII, 2 place Jussieu, F-75221 Paris Cédex 05, France

J. F. Morhange

Laboratoire de Physique des Solides, Université de Paris VI, 4 place Jussieu, F-75230 Paris Cédex 05, France (Received 23 October 1984)

Solid-phase crystallization kinetics of undoped, phosphorus-doped $(0 < [PH_3]/[SiH_4] < 2 \times 10^{-3})$, and boron-doped $(0 < [B_2H_6]/[SiH_4] < 2 \times 10^{-3})$ amorphous silicon films prepared by chemicalvapor deposition (CVD) of silane have been studied with use of conductivity measurements. The crystallization growth rates (V_g) and their activation energies (E_v) are obtained during isothermal annealings in a large temperature range $(510 < T_A < 650 \,^{\circ}\text{C})$. The growth rate is found to be enhanced as the doping content increases, whereas E_v remains almost constant $[E_v = (2.9 \pm 0.1) \, \text{eV}]$ in the entire doping range. The most striking point is that the increase of V_g is observed for relatively low doping concentrations and that there exists a simple correspondence between the increase of V_g and the decrease of the density of neutral dangling bonds measured by EPR. For boron doping the growth rate increases by a factor of 4 in the range $(0-7) \times 10^{-6}$ of diborane. In the same range, the neutral dangling bonds become positively charged and nonparamagnetic by electronic compensation with the acceptor atoms, and the EPR signal decreases from 10^{19} to 10^{17} spins/cm³. At higher doping concentrations, V_g remains constant except for the heavily doped sample, where an additional increase of V_g is observed. A similar behavior is obtained for phosphorus doping with a relatively small increase of V_g . We believe that these results indicate that dangling bonds play an important role in crystallization processes and the effect is dependent on their charge state. Possible models to account for this behavior will be discussed. X-ray-diffraction and Raman-spectroscopy measurements have also been carried out in order to control the crystallinity of the films.

I. INTRODUCTION

The crystallization kinetics of *a*-Si layers have been the subject of many studies using different techniques on materials prepared by several methods: evaporation, ion implantation, and glow discharge.¹⁻⁶ Many of these studies concern only undoped films and little has been done on the influence of doping on the crystallization process. Over the past several years, Csepregi *et al.*^{3,4} and, more recently, Lietoila *et al.*⁵ have investigated the effect of *n*-and *p*-type impurities on the rate of regrowth in materials amorphized by ion implantation. They observed an increase of the crystal growth rate (V_g) with increasing doping in both cases. For ³¹P-doping concentrations ranging from 0.9×10^{20} to 2.8×10^{20} cm⁻³, Csepregi *et al.*³ obtained an enhancement of V_g by a factor of about 6. The activation energy stays constant (2.35 eV) in this doping range. They also found that, for a doping level higher than 2×10^{20} cm⁻³, V_g remains constant. Lietoila *et al.*⁵ observed an increase of the activation energy cm⁻³. They observed a decrease of the activation energy ($E_v = 2.5 \text{ eV}$) with doping, compared with that found for impurity-free amorphous films ($E_v = 2.85$

eV). However, these papers concern heavily doped films, and a detailed study of the effect of the doping on solidphase epitaxial regrowth has not been yet presented. In addition, the authors of these papers studied heavily implanted samples in which the density of defects created by implantation can disturb the crystallization kinetics, as we will discuss later. On the other hand, these experiments cannot be correlated to transport and EPR results on the same films because they use a crystalline-silicon substrate.

The aim of this article is to present an extensive study of the solid-phase crystallization of undoped, borondoped, and phosphorus-doped amorphous-silicon films prepared by chemical-vapor deposition (CVD) of silane, on fused-silica substrates, during isothermal annealing treatments in a large temperature range, $510 < T_A$ < 650 °C. It has been suggested that defects such as vacancies or dangling bonds and their charge state play an important role in the crystal-growth mechanism.^{5,7} Furthermore, it has been shown that this charge state may be changed by doping or illumination.⁸ We will present here experimental results showing the effect of electrically active impurities (boron and phosphorus) on the growth rate (V_g) in a large doping range, with special interest on doping concentrations in which changes in the density of

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	Boron doping						Phosphorus doping		
Series number:	1	2	3	4	5	6	7	8	9
Boron or phophosrus concentration $C_{\rm B}$ or $C_{\rm P}$ ratios	undoped	$\frac{C_{\rm B}}{10^{-6}}$	$C_{ m B}$ 5×10 ⁻⁶	$\frac{C_{\mathrm{B}}}{7 \times 10^{-6}}$	$C_{\rm B}$ 2×10 ⁻⁵	$C_{\rm B}$ 2×10 ⁻³	$C_{\rm P}$ 2×10 ⁻⁵	$\frac{C_{\rm P}}{3\times10^{-4}}$	$C_{\rm P}$ 2×10 ⁻³
Temperature of deposition T_D (°C)	600	600	600	600	600	600	630	600	600
Thickness (µm)	1.3	0.88	0.95	0.8	0.7	1.1	0.56	0.16	0.42

TABLE I. Deposition conditions of the *a*-Si CVD films.

neutral dangling bonds are observed, and we will compare the increase of V_g to the density of unpaired spins measured by EPR. Possible models to account for this behavior will be discussed.

We will also present results obtained on structural properties studied by using x-ray-diffraction and Ramanspectroscopy techniques. They give complementary information about the crystallinity of the samples after the deposition or during the isothermal annealings.

II. EXPERIMENTAL SETUP

The amorphous films were prepared in a CVD reactor (Applied Material AMV 800) at atmospheric pressure. Pure silane (1 1/min) was diluted in hydrogen (32 1/min) in a vertical open-flow reactor with a silicon carbide susceptor heated by rf induction. We used fused-silica substrates held at 600 °C in order to obtain totally amorphous films.⁹ We also deposited films at temperatures ≥ 630 °C, which correspond to a partially crystallized layer.⁹ This point will be discussed in Sec. IV.

The substrates were carefully out-gassed and cleaned by *in situ* HCl etching at a relatively high temperature (1050 °C) prior to deposition. The thicknesses of the layers, from 560 to 1300 nm, were measured optically by standard transmission experiments. The doping is realized by addition of diborane or phosphine with silane in the gas phase during deposition. The boron- and phosphorus-doping concentrations defined by the ratios $C_{\rm B} = [B_2H_6]/[{\rm SiH_4}]$ and $C_{\rm P} = [{\rm PH_3}]/[{\rm SiH_4}]$ were within $0 \le C_{\rm B} \le 2 \times 10^{-3}$ and $0 \le C_{\rm P} \le 2 \times 10^{-3}$. The deposition



FIG. 1. (a) Schematic representation of a surface-induced crystallization (SIC). (b) Theoretical curve of $\Sigma(t)/\Sigma(t=0)$ vs time t following Eq. (1); the growth rate $V_g = e/\tau$, and τ is the crystallization time.

conditions are summarized in Table I for the different series of samples used (series 1-9). The crystallizationgrowth measurements were performed on as-deposited films isothermally annealed in an oven stabilized at ± 1 °C in a vacuum of about 10^{-6} Torr.¹ The variations of the electrical conductivity are measured in situ as a function of the annealing time.^{1,10} X-ray-diffraction measurements were carried out using a standard θ -2 θ Seifert MZ-IV step-by-step goniometer. Cu $K\alpha$ radiation and a scintillation detector were used. The experiments were performed in vacuum $(10^{-6}$ Torr), from room temperature up to 650 °C in a high-temperature chamber mounted on the θ circle of the goniometer. Raman-spectroscopy measurements are carried out at room temperature after successive annealings performed at a given temperature and for different annealing times. The excitation light is the 488-nm line of a 400-mW-power argon laser. This corresponds to a penetration depth δ in the *a*-Si layer of about 100 nm. The spectra are obtained using backscattering geometry. We measured the dependence of the crystalline Ramanpeak intensity with time. The principle of this technique is detailed in Refs. 11 and 12.

III. EXPERIMENTAL RESULTS

A. Determination of the growth rate of crystallization from conductivity measurements

On germanium and silicon, depending on the deposition conditions, different kinds of kinetics of solid-phase crystallization have been observed. The main cases are the bulk-induced crystallization (BIC) and the surfaceinduced crystallization (SIC). These cases have been extensively studied in previous papers.^{1,10} Amorphoussilicon CVD films studied in this paper show systematically a SIC.9 A fast nucleation at the substrate-film interface, which is predominant, occurs, and forms a starting polycrystalline layer near the silicon-substrate interface. This polycrystalline layer grows perpendicularly to this interface with a growth rate V_g , as shown in Fig. 1(a). In this case we determine directly and unambiguously the crystal-growth rate from the variation of the conductivity as follows: At a time t, the measured conductivity is that of two layers in parallel, the first being the polycrystalline layer of conductivity $\sigma_{\text{poly-Si}}$ and thickness $V_g t$, and the



FIG. 2. Variation of $\Sigma(t)/\Sigma(t=0)$ vs annealing time for an undoped sample of series 1, crystallized during isothermal annealing at 606 °C. τ is the crystallization time.

second the amorphous layer of conductivity $\sigma_{a-\text{Si}}$ and thickness $e - V_g t$, where e is the total thickness of the film [Fig. 1(a)]. The total conductance may be expressed as^{1,10}

$$\Sigma(t) = \Sigma(t=0) \left[1 + \left[\frac{\sigma_{\text{poly-Si}}}{\sigma_{a-\text{Si}}} - 1 \right] \frac{V_g t}{e} \right], \qquad (1)$$

where $\Sigma(t=0)$ is the conductance of the initial layer. The crystalline front reaches the free surface of the film at a time τ . We deduce that $V_g = e/\tau$ [Fig. 1(b)].







FIG. 4. Same variation for boron-doped sample at $C_{\rm B} = 5 \times 10^{-6}$ (series 3) crystallized at 600 °C.

B. Results

In Fig. 2 we present an example of the dependence of $\Sigma(t)/\Sigma(t=0)$ as a function of the annealing time for crystallizations, performed at 606 °C on an undoped sample (series 1). Figures 3 and 4 represent the same dependences for one phosphorus-doped film at $C_{\rm P}=3\times10^{-4}$ (series 8) and for a boron-doped film at $C_{\rm B}=5\times10^{-6}$ (series 3), respectively, both crystallized at 600 °C. The crystal-growth rates are deduced from these curves, as we have discussed in the preceding subsection, at different annealing temperatures and for the different series of samples.

In Fig. 5 the deduced V_g for undoped (series 1) and slightly-phosphorus-doped (series 7) samples, respectively,



FIG. 5. Variation of $\log_{10}V_g$ vs reciprocal temperature obtained for samples crystallized during isothermal annealing: undoped samples (\times, \ast, \circ) (series 1); very slightly doped samples at $C_{\rm P} = 2 \times 10^{-5}$ (\bullet) (series 7); data deduced from x-ray measurements (\oplus) (see Fig. 8).

	Undoped			Boron doping			P	hosphorus doping	
Series number:	1	2	3	4	5	9	L	8	6
Vg at 600°C									
Å/s)	1.25	1.45	2.7	4	3.9	6.7	1.25	1.9	1.3
V _g at 550°C									
Å/s)	1.1×10^{-1}	1.45×10^{-1}	3.2×10^{-1}	4.1×10^{-1}	3.8×10^{-1}	5.9×10^{-1}	1.1×10^{-1}	1.8×10^{-1}	4×10^{-2}
spin density (spins cm ⁻³)							• *		
or $g = 2.0055$	10 ¹⁹	6.5×10^{18}	4×10^{18}	1.4×10^{18}			1019	1017	
E_{v} (eV)	2.9	2.9	2.9	2.8	2.8	ŝ	2.9	3	4.1



FIG. 6. Comparison of growth rates V_g obtained for undoped sample (---), with those obtained for boron-doped samples at various doping concentrations: \bigcirc , $C_{\rm B}=10^{-6}$; \bullet , $C_{\rm B}=5\times10^{-6}$; +, $C_{\rm B}=7\times10^{-6}$; \triangle , $C_{\rm B}=2\times10^{-5}$; *, $C_{\rm B}=2\times10^{-3}$.

are shown as a function of the reciprocal temperature. We compare, in Figs. 6 and 7, the growth rates measured in boron-doped (series 2–6) and phosphorus-doped samples (series 8), respectively, with that of undoped films⁹ (series 1). The experimental values of V_g are indicated in Table II for two annealing temperatures, 550 and 600 °C.

We have also measured the crystal-growth rate by performing x-ray experiments.¹³ In Fig. 8 we present one example of the dependence of the Bragg-peak intensity on the (111) crystalline planes as a function of the annealing time at 627 °C on undoped samples (series 1). The crystallization time τ and the crystal growth rate V_g are obtained in a similar way as was done previously for conductivity measurements. The V_g deduced by this new method, at 627 °C, is shown in Fig. 5.



FIG. 7. Comparison of V_g obtained for undoped samples (--) (series 1) with that obtained for a phosphorus-doped sample at $C_P = 3 \times 10^{-4}$ (\bullet) (series 8).



FIG. 8. Variation of the Bragg-peak intensity vs annealing time for undoped sample (series 1) crystallized during isothermal annealing at 627 °C

Moreover, one amorphous-silicon layer of series 1 has been crystallized during isothermal runs at 590°C, and Raman spectra were obtained at different annealing times. The results are summarized in Figs. 9, 10, and 11, which correspond to annealing times of 2, 5, and 7 h, respectively. These times correspond to three stages in crystallization: the beginning of the linear dependence in the conductivity curve, the middle of the linear variation, and the saturation region, respectively. Panels (a) and (b) of each figure correspond to light incident on the free surface of the layer and through the substrate, respectively. The Raman spectra clearly show that during the annealing experiments the crystallization takes place first at the substrate-film interface:¹⁴ In Fig. 9 we observe the appearance of the crystalline peak ($\sim 520 \text{ cm}^{-1}$) from incident light through the substrate [Fig. 9(b)]. This peak increases with annealing time [Figs. 10(b) and 11(b)]. On the other hand, for light incident on the free surface, the broad peak near 480 cm⁻¹ characteristic of the amorphous structure is observed [Figs. 9(a) and 10(a)]. It is re-



FIG. 9. Raman-scattering intensity as a function of frequency for undoped film (series 1) annealed at 590 °C for a time t=2 h. (a) Light incident on the free-surface side; (b) light incident through the substrate.



FIG. 10. Raman spectra after an annealing time t=5 h at 590 °C.

placed by the crystalline peak at the end of crystallization [Fig. 11(a)].

IV. DISCUSSION

Figures 2-4 clearly show that, experimentally, we do not observe a linear variation of the conductivity for the entire annealing time, as has been predicted by Eq. (1) and Fig. 1(b). At the beginning of the crystallization process, it appears to be a departure from the linear dependence. We correlate this behavior as being due to the existence of an "initiation" or "transit" time τ_1 of crystallization. This initiation time is always observed, except for crystallization at temperatures T > 700 °C, where it is too small to be experimentally seen. $\widetilde{W}e$ interpret this initiation time τ_1 as being the time necessary to form a continuous polycrystalline layer at the amorphous-substrate interface (see Raman experiments, Fig. 9). The same initiation time is also observed in the dependence of the x-ray-diffraction intensity with time (Fig. 8). We estimate, by these measurements, the thickness of the polycrystalline layer at the



FIG. 11. Raman spectra after an annealing time t=7.5 h at 590 °C.

interface to be of the order of 100 nm. The initiation time is found to be dependent on the annealing temperature of crystallization for each series of samples (Fig. 12). It depends also on deposition conditions, mainly temperature of deposition. We observe, for example, a longer time τ_1 for samples deposited at 600 °C (series 1) than for samples deposited at ~630 °C (series 7), where a polycrystalline layer is present at the substrate-film interface in asdeposited films⁹ (Fig. 13). The dependence of the initiation times τ_1 , as a function of the reciprocal temperature, is presented in Fig. 14 for samples denoted by series 1 and 7, respectively. This figure shows that the initiation time is thermally activated, with an activation energy equal to 2.9 eV. This value is almost the same as that of the growth rate V_g ,^{5,15} as has been explained by the theory of transient nucleation reviewed in Ref. 7.

Concerning the linear region in the plot of crystallization versus time, x-ray measurements give direct information on the crystallized volume, the grain size, and the preferred orientation of the crystallites. During the isothermal annealing experiments we obtain systematically, at each time t, a polycrystalline layer with a $\langle 111 \rangle$ preferred orientation of the crystallites. The average grain size measured in our samples is about 60 nm.

Figure 15 summarizes, on undoped and slightly doped samples, series 1 and 7, the results obtained on V_g . It shows that the growth rate is thermally activated $[V_g = V_0 \exp(-E_v/k_BT)]$, with an activation energy $E_v = (2.9 \pm 0.1)$ eV. It also shows that a phosphorusdoping concentration of $C_P = 2 \times 10^{-5}$ does not affect V_g at all. The values obtained in this case for V_g and E_v are in agreement with previous results obtained on evaporated a-Si.¹ The measured values of V_g are very close to those reported on self-implanted silicon^{5,16} in the (111) crystal direction, as we expected from the x-ray preferredorientation study. For other directions of crystal growth



FIG. 12. Variation of $\Sigma(t)/\Sigma(t=0)$ vs annealing time for samples of series 7 in order to show the different transient times τ_1 corresponding to different annealing temperature: +, 580°C; \circ , 600°C.



FIG. 13. Variation of $\Sigma(t)/\Sigma(t=0)$ vs annealing time for crystallization performed at 606 °C in order to show the different transient times τ_1 corresponding to different kinds of samples: +, samples deposited at 600 °C (series 1); \odot , samples deposited at ~630 °C (series 7).

 $(\langle 110 \rangle \text{ and } \langle 100 \rangle)$, these authors have reported V_g values 10 and 30 times higher. In all these papers the activation energy of undoped or self-implanted samples is the same, independently of the preparation method and the crystal-growth direction. However, Csepregi *et al.*³ have reported a lower value of E_v (2.35 eV) from earlier measurements on ion-implanted silicon impurity-free films.

On the other hand, Fig. 6 shows that the main effect of



FIG. 14. Variation of the transient time vs reciprocal temperature for different series of samples crystallized at different annealing temperatures: +, samples of series 1 deposited at 600 °C; \circ , samples of series 7 deposited at ~630 °C.



FIG. 15. Variation vs boron-doping concentration of the spin density of neutral dangling bonds at g=2.0055 and the ratio $V_g(C_B)/V_g(C_B=0)$ obtained at 550 and 600 °C.

the doping is the enhancement of V_g with increasing doping concentration. V_g increases by about a factor of 4 when C_B changes from 0 up to $C_B = 7 \times 10^{-6}$, and then we obtain a saturation for higher concentration, except for the heavily doped sample ($C_B = 2 \times 10^{-3}$), where a small additional increase of V_g is observed. The associated activation energy E_v remains almost constant over the entire doping range. We may define a common activation energy $E_v = (2.9 \pm 0.1)$ eV to be equal, within the experimental error, to that of undoped films.

For phosphorus doping, Fig. 7 shows that a similar enhancement of V_g is also obtained for $C_P = 3 \times 10^{-4}$, but the effect is smaller than that observed in the boron case. We obtain the same activation energy $(E_v = 2.9 \text{ eV})$, except for the heavily doped sample $(C_P = 2 \times 10^{-3})$, which corresponds to a higher value of E_v $(E_v = 4.1 \text{ eV})$. All of these experimental values are summarized in Table II.

A similar behavior of the enhancement of V_g versus doping has been reported by other authors.^{3,5,18} Only high doping levels of both *n*- and *p*-type impurities have been investigated by these authors [in the range $(1-2.5)\times10^{20}$ impurity atoms cm⁻³] and, in their cases, they observed a variation of the activation energy E_v versus doping. Csepregi *et al.*³ obtained $E_v = 2.35$ eV for the undoped case, as compared with that of the phosphorus-doped sample $(2.8\times10^{20} \text{ cm}^{-3})$, 2.5 eV. The enhancement of V_g is about a factor of 6, much larger than in our case. In the case of boron doping $(2.5\times10^{20} \text{ cm}^{-3})$, these authors obtained a much higher enhancement of V_g (factor of ~25), but the activation energy decreases to about $E_v \approx 1.9 \text{ eV}$. It is difficult in their case to assign an accurate activation energy for the doped samples because the doping concentration varies strongly with depth.³

Lietoila et al.⁵ obtained, for undoped and compensated $({}^{11}\text{B} + {}^{31}\text{P}\text{-doped})$ samples, almost the same V_g and E_v (2.8 eV). For a phosphorus-doped sample $(1.7 \times 10^{20} \text{ cm}^{-3})$, they reported an enhancement of V_g by a factor of 10, and $E_v = 2.5 \text{ eV}$. In this case the homogeneity of the doping concentration is better controlled than in the previous case.

The change in the activation energies observed by these authors in heavily doped samples could be explained partially by alloying effects at these doping levels. This could be also the case of our heavily-phosphorus-doped sample ($E_v = 4.1 \text{ eV}$).

In the moderate doping range, which we treated here, there is no change in E_v , and we will give an interpretation of the increase of V_g with doping without considering any alloying effect. Several models have been proposed to explain the enhancement of V_g : For one, it can be related to a stress caused by the mismatch between the impurity and the host atoms. This model can be ruled out by considering that only electrically active atoms give an enhancement of V_g ,¹⁸ and the fact that, in compensated materials, V_g is very close to that of undoped films.⁵ Other models associate the increase of V_g with an electrical phenomena related to a shift of the Fermi-level position.^{3,5,18}

In these models, growth rates depend on the number of vacancies and their charge states. According to Van Vechten et al.,^{19,20} the number of these charged vacancies increases when the Fermi level moves up or down from the midgap position. As dangling bonds are more common defects than vacancies in amorphous silicon,¹⁵ we think that these dangling bonds may play a similar role in the crystallization mechanism.⁷ In order to clarify this assumption, we compare, in Fig. 15, the variation of V_g and the spin density of unpaired dangling bonds, measured by EPR at room temperature with a Landé factor g=2.0055, versus the boron-doping concentration.²¹ This figure shows a clear correlation between the increase of the growth rate V_g and the decrease of the density of neutral dangling bonds in the same boron-doping range. The crystal-growth rate saturates when no EPR signal at g=2.0055 is detected (Table II). The decrease of the density of neutral dangling bonds with increasing doping has been interpreted as the following:⁸ In the case of boron doping, the electrically active boron atoms compensate for the neutral and paramagnetic dangling bonds, with charge state D^0 , by changing their charge states following the reaction $D^0 + B \rightarrow D^+ + B^-$, where D^+ is the positively charged, nonparamagnetic, dangling-bond state. We may explain in the same way the decrease of the density of neutral dangling bonds with increasing phosphorusdoping concentrations⁸ by the reaction $D^0 + P \rightarrow D^ + P^+$, where D^- is the negatively charged, nonparamagnetic, dangling-bond state.

The clear correlation obtained between the dependence of V_g and the spin density on doping (Fig. 15) shows that dangling bonds⁷ rather than vacancies are involved in the crystal-growth mechanism, and that the change of their charge states is responsible of the enhancement of the crystal-growth rate with doping, for both boron and phosphorus doping.

Germain *et al.*⁷ have proposed a model to explain both the ionization and doping enhancement of V_g in amorphous Ge and Si. This model assumes that (i) dangling bonds diffuse from the bulk towards the amorphouscrystalline interface; this assumption is in agreement with the results of Thomas *et al.*¹⁷ obtained for evaporated amorphous silicon; (ii) only certain sites on the amorphous side of the interface are available for crystallization, and these sites are those which have captured dangling bonds; (iii) the capture cross section at the interface depends on the charge state of the dangling bonds and modifies the growth rate at this interface. One important conclusion⁷ of this model is that the activation energy of the crystalgrowth rate remains roughly constant in the considered doping range, as has been experimentally observed.

V. CONCLUSION

Crystal-growth rates during solid-phase crystallization have been measured in a large temperature and doping ranges on *a*-Si CVD films. A detailed study of the crystallization is given by using conductivity, x-ray, and Raman-scattering measurements. An "initiation" time at the beginning of the crystallization is discussed in detail for undoped samples. Concerning the results of V_g versus doping, we point out our particular interest on doping concentrations in which the density of neutral dangling bonds measured by EPR at g=2.005 decreases with increasing doping concentration. We have shown a clear correlation between the enhancement of the growth rate V_g and the decrease of the spin density. The activations energy of V_g remains almost constant over the entire doping range. These experimental results show that dangling bonds and their charge states play an important role in the crystallization process, as has been previously proposed.⁷

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