

Transition from anomalous kinetics toward Fickian diffusion for Si dissolution into amorphous Ge

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Over the last years, several experimental and theoretical studies of diffusion kinetics on the nanoscale have shown that the time evolution ($x \propto t^{k_c}$) differs from the classical Fickian law ($k_c=0.5$). However, all work was based on crystalline samples or models, so far. In this letter, we report on the diffusion kinetics of a thin amorphous Si layer into amorphous Ge to account for the rising importance of amorphous materials in nanodevices. Employing surface sensitive techniques, the initial k_c was found at 0.7 ± 0.1 . Moreover, after some monolayers of Si dissolved into the Ge, k_c changes to the generally expected classical Fickian law with $k_c=0.5$. © 2008 American Institute of Physics. [DOI: 10.1063/1.2908220]

Studies of diffusional movement of atoms through interfaces and of the resulting interface shift are nowadays of great interest not only from a fundamental research point of view (the search of diffusion laws valid on the nanoscale) but they are of practical importance as well. Recent progress in device technology allows us to directly approach structures on the nanoscale, for which the knowledge of the corresponding diffusion laws is indispensable. Also, related to this topic is the possible degradation of parts of electronic devices being often due to material transport through interfaces. Accordingly, in order to extend the lifetime of such devices a detailed understanding of the underlying diffusion processes is required.

During the past years, several publications dealt with anomalous diffusion in different systems (e.g., Refs. 1–5). Some of them showed that during the dissolution of a thin film into a single crystalline substrate, the shift of the interface was proportional to t^{k_c} , where t is the time. The value of k_c kinetic exponent was not always equal to 0.5 (Fickian diffusion). Depending on two parameters, k_c was between 0.25 and 1 (e.g., Refs. 6–8). These parameters were the diffusion asymmetry parameter m' , which measures the difference between the diffusivities in the film and the substrate in orders of magnitude, and the mixing energy V determining the phase separation tendency.

It is important to note that there are numerous other examples of experimentally observed nonparabolic growth kinetics in the literature. However, in all of these cases, the linear growth of phase(s) in solid state reactions was interpreted as a consequence of the reaction rate control at the interface(s).^{9–12} Here, it is also worth noting that strong diffusion asymmetry may lead not only to sharp interface shift

with anomalous kinetics on the nanoscale but to sharpening of an initially diffuse interface even in completely miscible systems.^{13,14}

However, in the above studies, k_c has not been determined either from computer simulations or experiments in amorphous systems although they play more and more important roles in applications. With an ever increasing importance of amorphous materials in nanoscale applications due to their useful optical and electronic features,^{15,16} it is an important question whether anomalous diffusion can be experimentally observed in amorphous systems as well.

To answer this question, Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were carried out on the dissolution of a thin (~ 3 nm for AES and ~ 1 – 4 nm for XPS experiments) amorphous Si layer into a thick (~ 100 nm) amorphous Ge layer. From isothermal heat treatments, the corresponding kinetic exponents were determined. Germanium layers with a thickness of 100 nm were prepared at room temperature by magnetron sputtering. The quality of the Ge surface was checked by atomic force microscopy revealing a mean roughness below 1 nm for typical scan lengths of 1000 μm .

For AES investigations, the native Ge oxide layer was removed by ion bombardment followed by annealing the samples for 1 h at 573 K. The 3 nm thick Si top layers were prepared by thermal evaporation. The absence of the Ge (52 eV) peak indicated a complete coverage by the Si top layer. The experiments were performed under ultrahigh vacuum (UHV), using an electron beam as primary excitation source. The beam energy was set to 2050 eV and the beam current was set to 105 μA during the whole experiment. Auger electrons were detected using a cylindrical mirror analyzer. The sample temperature was measured and regulated via a platinum-rhodium thermocouple placed on the surface of the sample. Both the Ge LMM transition at 1147 eV and the Si LMM transition at 92 eV were simultaneously recorded *in situ*. The Si transition corresponds to an

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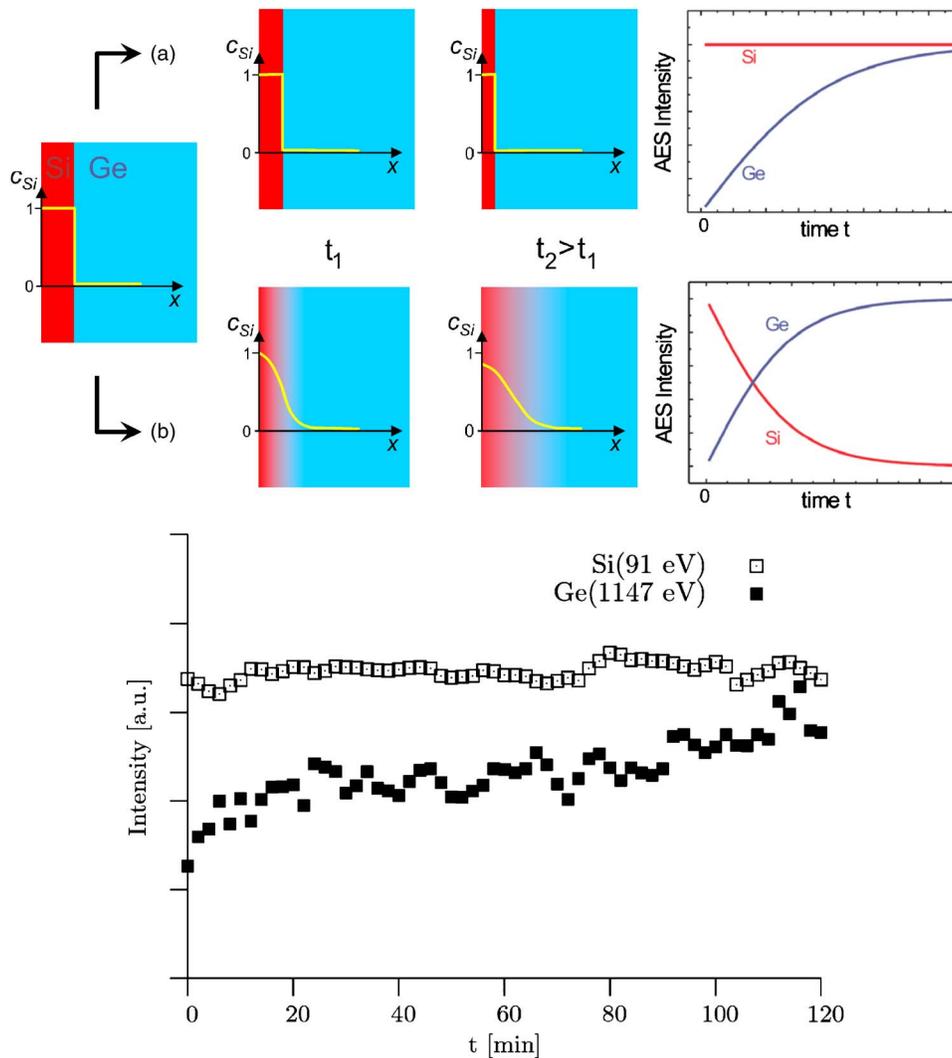


FIG. 1. (Color online) Upper panel: two possible scenarios for the initial part of the Ge LMM and Si LMM AES signal intensity vs time recorded at fixed temperature. (a) The interface remains sharp. (b) There is an interface broadening during intermixing; the yellow curves show the Si composition profiles around the Si/Ge interface. Lower panel: experimental curve at 623 K. The Ge signal increases, whereas the Si remains constant, which indicates that the interface remains abrupt during the process.

inelastic mean free path (IMFP) of 0.5 nm while the Ge transition corresponds to an IMFP of 2.5 nm (the IMFP was calculated from Ref. 17).

In the upper panel of Fig. 1, two possible interdiffusion scenarios are schematically given. Scenario (a) assumes a strong diffusional asymmetry with Si being a fast diffusant within amorphous Ge but not vice versa. In this case, a sharp Si/Ge interface can be conserved. Scenario (b) assumes a more symmetric diffusion leading to a broadening of the interface. Both assumptions result in a characteristic time dependence of the AES signals. Since the Si LMM Auger electrons have a very short IMFP in Si ($\lambda_{\text{Si}} \approx 0.5$ nm, see, e.g., Ref. 17) whereas the Ge LMM electrons exhibit a much larger value ($\lambda_{\text{Ge}} \approx 2.5$ nm, see, e.g., Ref. 17) in Si, one expects for the sharp interface scenario a temporal increase in only the Ge signal while the Si signal remains constant until the Si thickness approaches the limit of about $2\lambda_{\text{Si}}$ [Fig. 1(a)]. In the case of interface broadening, Ge reaches the surface quite fast resulting in an immediate decrease in the Si signal. This decrease would be much more pronounced than the increase in the Ge signal since the AES is much more sensitive for Si than for Ge [Fig. 1(b)]. The corresponding experimental data are also presented in the lower panel of Fig. 1, where the temporal evolution of the Si and Ge AES signals are given. Comparing this to scenarios (a) and (b), it is clear that the experiment is in favor of a conserved sharp Si/Ge interface during the observation time of 2 h. Thus, the

present data corroborate the idea that the Si/Ge interface remains abrupt during diffusion as had been concluded from earlier Auger depth profiles.¹⁸ Using the IMFP data, it is possible to calculate a kinetic exponent (see in Ref. 6) of $k_c \approx 0.7$.

In order to refine the above results, XPS measurements were performed allowing quantitative analysis. For the XPS experiments, the Ge specimens were dipped into 2% HF for 15 s. After cleaning in de-ionized water, the samples were stored in ethanol before transferring them into the UHV system. After additional annealing at 473 K for 2 h, the Ge surfaces were found to be completely free of any oxide. Subsequently, the 1–4 nm thick Si layers were prepared by e-beam evaporation *in situ*. In this case, ultraviolet photoelectron spectroscopy (UPS) was applied for testing complete coverage by the Si layer since low energy photoelectrons excited by UPS have very low IMFP. In the measurements, we used an Al $K\alpha$ source (nonmonochromatized) with the electrons detected by a MCD 100 multichannel detector (SPECS). To monitor the Si/Ge interdiffusion, the Ge $2p_{3/2}$ peak, the Ge $3p$ doublet and Si $2s$ peak were recorded. To account for maximum intensity (for faster recording), we used a pass energy of 100 eV. The temperature was set to 603 K and controlled by a pyrometer.

In evaluating the XPS spectra, the results of the AES measurements were used, i.e., it was assumed that the interface remains sharp during the diffusion. Thus, from change

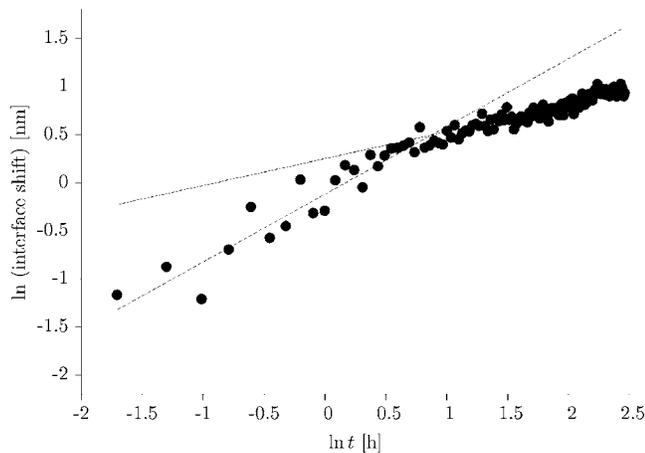


FIG. 2. Interface shift (initial minus apparent thickness of the Si film) vs time on log-log scale. The non-Fickian first part as well as the transition are clearly visible. (The dashed straight line is fitted to the first anomalous part of the data, whereas the solid one to the last Fickian part.)

of Ge $2p$ /Ge $3p$ signal ratio, the decrease in the silicon thickness due to its diffusion into the underlying Ge layer could be determined. In order to finally extract the kinetic coefficient k_c , the position of the interface (initial Si thickness minus the apparent Si thickness) is plotted versus time on a log-log scale in Fig. 2. Since a power function is linear in this representation, the slope is just equal to the exponent: $x \propto t^{k_c} \Rightarrow \ln(x) \propto k_c \ln(t)$.

As can be seen, in Fig. 2, in order to fit the data points, two straight lines are needed. This means that k_c is not a constant but changes in time. In this way, an initial and final values of k_c could be determined resulting in 0.7 for the initial and 0.53 for the final value. Thus, one concludes that the process anomalously starts (in non-Fickian way) but returns to the Fickian behavior for longer times.

Table I summarizes the results obtained in the initial stage of the different measurements. It is clearly visible that the measured kinetic exponents agree quite well. Their values around 0.7 indicate that a large diffusional asymmetry causes the non-Fickian interface shift just like in crystalline systems. The column “transition length” gives the approximate Si length dissolved into Ge for which an anomalous diffusion with exponent $\approx 0.7 \pm 0.1$ could be measured.

TABLE I. Results from different measurements. The last column gives the dissolved Si layers for which the kinetic exponents have been evaluated.

Sample. No	Method	Exponent	Transition Length (nm)
1	AES	0.7	>1.25
2	XPS	0.65	>0.5
3	XPS	0.72	0.75
4	XPS	0.70	1.75
5	XPS	0.68	1.25

Clearly, the diffusion anomaly is restricted to 1–2 nm (a few monolayers) of Si and only after the dissolution of more layers the diffusion kinetics returns to the classical Fickian law.

In this paper, an experimental proof of non-Fickian diffusional kinetics in amorphous materials is provided. The present results together with those obtained for crystalline systems demonstrate that asymmetric diffusion causes deviation from the classical diffusion kinetics on the nanoscale, independent of the material structure and diffusional mechanism (the diffusion mechanism is different in the amorphous and crystalline Si/Ge system¹⁹). Therefore, anomalous diffusion due to diffusion asymmetry appears as a fundamental phenomenon in nature.

Moreover, in the present work, not only the anomalous part of the diffusion process could be observed but also the transition back to the classical Fickian behavior.

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