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Citation: Applied Physics Letters **75**, 3515 (1999); doi: 10.1063/1.125373
View online: http://dx.doi.org/10.1063/1.125373
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APPLIED PHYSICS LETTERS VOLUME 75, NUMBER 22 29 NOVEMBER 1999

Low-temperature growth of crystalline silicon on a chlorine-terminated surface

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(Received 13 July 1999; accepted for publication 7 October 1999)

We report on the role of surface termination during growth of crystalline silicon at low temperatures. Microcrystalline silicon was fabricated using plasma-enhanced chemical-vapor deposition with a hydrogen-diluted dichlorosilane (SiH_2Cl_2)/monosilane (SiH_4) mixture to study the role of hydrogen and chlorine in crystal formation. When varying the fraction of SiH_2Cl_2, $x = [SiH_2Cl_2]/([SiH_4]+[SiH_2Cl_2])$, good crystallinity was obtained for $x=0$ and 1, whereas the crystallinity was markedly deteriorated for intermediate x. Optical emission spectroscopy of the plasma suggests that film precursors different from SiH_x fragments and atomic chlorine are generated for $x \neq 0$ and that atomic hydrogen is generated in all cases. Infrared reflection absorption spectroscopy indicates that the surface coverage is hydrogen for $x=0$, chlorine for $x=1$, and a hydrogen–chlorine mixture for intermediate x. These results imply that low-temperature growth of crystalline silicon is facilitated on a chlorine-terminated surface as well as on a hydrogen-terminated surface under the presence of atomic hydrogen. The cooperative roles of chlorine and hydrogen are proposed in the crystal growth of Si. © *1999 American Institute of Physics.*
[S0003-6951(99)01648-4]

Low-temperature growth ($T < 450\,°C$) of crystalline silicon is of intense interest from the viewpoint of applications to low-cost devices on glass substrates, such as solar cells and thin-film transistors. Plasma-enhanced chemical-vapor deposition (PECVD) has been widely used for the growth of crystalline silicon with a SiH_4/H_2 gas mixture at 13.56 MHz. Although the mechanism of crystal formation at low temperatures is still controversial,[1–4] hydrogen is considered to play an important role in the formation mechanism. On the other hand, as an alternative method, dichlorosilane (SiH_2Cl_2) and tetrafluorosilane (SiF_4) source gases have been examined with the addition of hydrogen.[5–7] A growing surface when using SiH_4/H_2 has been studied by infrared reflection absorption spectroscopy (IRRAS),[8] whereas less knowledge has been obtained upon growth in halogen cases.

In this letter, we report a study of crystalline silicon growth at temperatures of 200–350 °C using rf-PECVD with a $SiH_4/SiH_2Cl_2/H_2$ gas mixture to clarify the role of halogens and hydrogen in crystal growth. It was found that either a SiH_4/H_2 or SiH_2Cl_2/H_2 source gas mixture results in crystal formation and that a mixture of SiH_4 and SiH_2Cl_2 deteriorates the crystallinity. The surface termination was identified to be halogen in the SiH_2Cl_2/H_2 case using IRRAS observation. Crystal formation on a halogen-terminated surface is discussed in relation to the hydrogenated surface.

Crystalline Si films have been deposited on glass substrates from dichlorosilane (SiH_2Cl_2)/monosilane (SiH_4) mixtures diluted by H_2 using a conventional rf-PECVD method. The crystallinity of the samples was evaluated from a Raman spectrum by taking the ratio of the signal height for the crystalline peak at 520.5 cm^{-1} to the amorphous peak at 480 cm^{-1}. Optical emission spectroscopy (OES) of the plasma was performed to investigate generated radicals in the plasma using a highly sensitive charge-coupled device camera (Princeton Research i-max 500). Surface termination was observed using infrared reflection absorption spectroscopy.

Figure 1 shows the deposition rate and crystallinity as a function of the SiH_2Cl_2 fraction, $x = [SiH_2Cl_2]/([SiH_4]+[SiH_2Cl_2])$, maintaining the flow rates of $[SiH_4]+[SiH_2Cl_2]$ and $[H_2]$ constant at 10 and 390 sccm, respectively. The growth temperature was 350 °C. As reported elsewhere,[9] a high deposition pressure of 4 Torr was used in this study, and thereby a deposition rate of 8 Å/s was obtained for $x=0$. With increasing x, the growth rate is slightly increased and the crystallinity deteriorates abruptly.

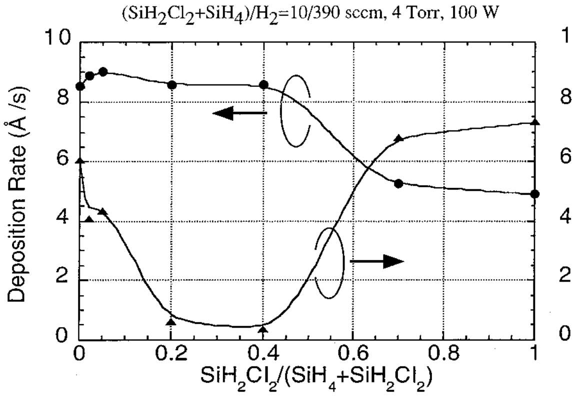

FIG. 1. Growth rate and Raman crystallinity as a function of dichlorosilane fraction, $x = [SiH_2Cl_2]/([SiH_2Cl_2]+[SiH_4])$. The Raman crystallinity was obtained from the ratio of the intensities at 520 cm^{-1} (c-Si phase) to the value at 480 cm^{-1} (a-Si phase), I_c/I_a. The total flow rate of SiH_4 and SiH_2Cl_2 was 10 sccm, hydrogen flow rate 390 sccm, total pressure 4 Torr, and rf power 100 W applied to a cathode 10 cm in diameter.

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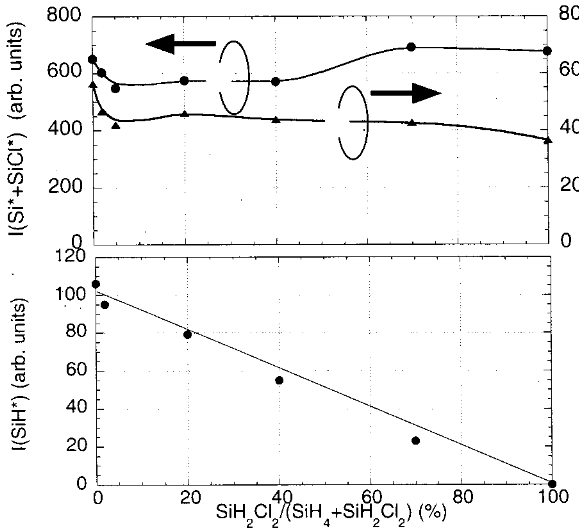

FIG. 2. Optical emission intensity from the plasma as a function of dichlorosilane fraction, $x=[SiH_2Cl_2]/([SiH_2Cl_2]+[SiH_4])$ in percent for H_α (655 nm), Si* (SiCl) (288 nm), and SiH* (414 nm) lines. Experimental conditions for the plasma were the same as those for Fig. 1.

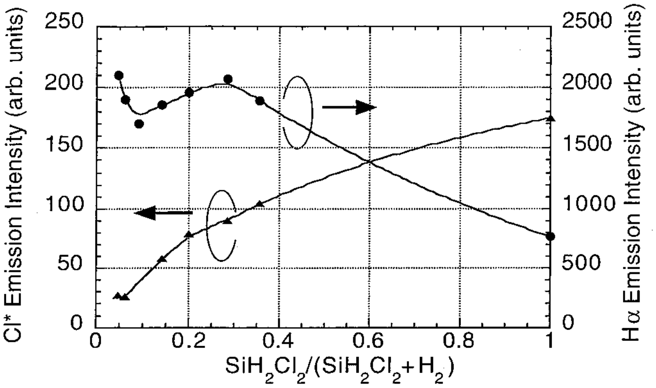

FIG. 3. Optical emission intensity from the plasma as a function of the SiH_2Cl_2 fraction for the Cl* (755.4 nm) and H_α (655 nm) lines. The flow rate of SiH_2Cl_2 was constant at 10 sccm, and only the hydrogen flow rate was varied. Total pressure was 0.4 Torr, and rf power 20 W.

For intermediate fractions, $x=0.2$ and 0.4, no crystalline phase appeared. Increasing x greater than 0.5 results in a reduction in the growth rate, which may be attributed to higher dissociation energy of SiH_2Cl_2 than SiH_4, and a crystalline phase appears again. For $x=1$, the crystallinity is higher than that for $x=0$.

OES measurements were carried out for various dichlorosilane fractions x, and we monitored several lines related to Si* (or SiCl*) (288 nm), SiH* (414 nm), H_α (656 nm), and Cl* (755 nm). Since Si* and SiCl* lines have almost identical photon energies, the line at 288 nm may contain the contribution of both the Si* and SiCl* lines. Figure 2 shows the SiH_2Cl_2 fraction dependence of Si*, SiH*, and H_α emission intensities $I(\text{Si*}, \text{SiH*}, H_\alpha)$. The spatial distribution of emission intensity is integrated over the electrode spacing to obtain $I(\text{Si*}, \text{SiH*}, H_\alpha)$. With increasing x, the $I(H_\alpha)$, and $I(\text{Si*})$ are almost constant, and only the $I(\text{SiH*})$ decreases linearly. For $x=1.0$, the growth rate was proportional to $I(\text{Si*}+\text{SiCl*})$ emission intensity, but not to the $I(\text{SiH*})$. This is different from the pure silane ($x=0$) case.[10] When varying the hydrogen dilution ratio of dichlorosilane, the $I(\text{Cl*})$ increases with increasing SiH_2Cl_2 fraction, while the $I(H_\alpha)$ decreases, as shown in Fig. 3. These OES results suggest the coexistence of atomic chlorine and hydrogen and their competing reaction on the growing surface depending on x.

Surface diagnosis using IRRAS has been carried out to identify the surface-termination species in a different apparatus under identical conditions to those for these depositions. First, a SiH_2Cl_2/H_2 mixture (2/100 sccm, 350 mTorr, 240 °C) plasma was operated to grow the film. IRRAS spectra of a chlorinated surface were observed during the growth [Fig. 4(a)], as well as after the growth [Fig. 4(b)]. Then, several monolayers were deposited at $x=0$ [Fig. 4(c)] to achieve a totally hydrogenated surface. Finally, deuterium plasma exposure was performed to completely exchange the surface hydrogen with deuterium, so the last IR spectrum was used to normalize all the previous spectra. As a result, Si–D_x bands at around 1500 cm^{-1} are seen as upward peaks. For $x=0$, the surface is mostly terminated by hydrogen as reported before.[8] For $x=1$, we could not observe surface hydrogen at all, but did observe surface Si–Cl around 600 cm^{-1}. These surface diagnosis results and their relevance to the crystallinity shown in Fig. 1 suggest that a growing surface covered by chlorine facilitates crystal growth as well as a hydrogen covering surface.[10] We also confirmed that coexisting hydrogen and chlorine termination disrupt the crystal growth. Since the growth temperature in this work is much lower than the thermal desorption threshold of hydrogen–halogen-related species from the crystalline silicon surface,[11] the surface dangling bonds are expected to be mostly terminated by chlorine for $x=1$.

The surface termination under the coexistence of atomic hydrogen and chlorine flux was studied using molecular beams generated by pyrolisis of H_2 and Cl_2 gases, respectively,[12] and it was reported that the surface termination at room temperature is mostly chlorine, which is consistent with the IRRAS results in this work, although a difference in the flux density of hydrogen and chlorine and in substrate temperature should be taken into account.

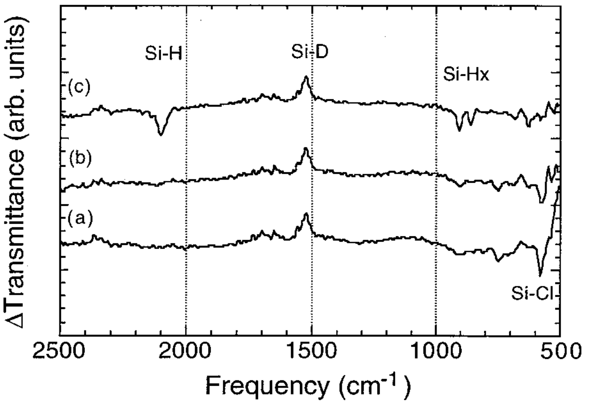

FIG. 4. Infrared absorption spectra observed by an IRRAS technique for (a) the growing surface during deposition with dichlorosilane, (b) the surface after the growth of (a), and (c) the hydrogenated surface after deposition with silane. All the spectra were normalized by the spectrum for the deuterated surface (not shown).

A correlation between crystal formation and surface hydrogen coverage has been pointed out in the silane case ($x=0$).[2,10] On a surface partly terminated by hydrogen at high temperatures, the crystallinity is deteriorated.[10] In addition, in molecular beam epitaxy of silicon, the crystallinity deteriorates with surface hydrogen coverage.[13] These results have a common aspect with the results in the present study: Crystal growth is facilitated on a ''homogeneous'' surface but disrupted on an ''inhomogeneous'' surface. In crystal growth, adsorbates on the surface should find an energetically stable site to form a crystalline network through surface diffusion. If the surface is inhomogeneous, adsorbates will suffer from having different energy barriers during diffusion, resulting in a reduced diffusion length, i.e., a kind of localization takes place. Since hydrogen dilution is necessary even in the dichlorosilane process, we suggest a cooperative effect of atomic hydrogen flux onto the surface and chlorine termination in crystal formation at low temperatures.

In summary, we have provided evidence of the enhanced growth of crystalline silicon on a chlorine-terminated surface at low temperatures. The mechanism of the chlorine termination and its beneficial role are discussed in terms of the surface chemistry, and a similarity to the growth on a hydrogenated surface is also discussed.

One of the authors (L.G.) would like to thank the New Energy and Industrial Technology Development Organization (NEDO) for their support of this work through a fellowship.

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