Doping by metal-mediated epitaxy: Growth of As delta-doped Si through a Pb monolayer

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In molecular-beam epitaxy a monolayer of Pb on the Si(111) surface induces single-crystal growth at temperatures well below those required for similar growth on a bare surface. We demonstrate that the suppression of dopant segregation at the lower temperatures attainable by Pb-mediated growth allows the incorporation of As donors at concentrations reaching a few atomic percent. When Pb and Si are deposited on an As-terminated Si(111) substrate at 350 °C, the Pb segregates to the surface without doping the Si film while the As is buried within nanometers of the substrate–film interface. The resulting concentration of electrically active As, 1.8×10^{21} cm^{-3}, represents the highest concentration of As donors achieved by any delta-doping or thin-film deposition method.
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Enabling the deposition of materials a monolayer at a time, molecular-beam epitaxy (MBE) is the natural choice for the growth of semiconductor thin films with delta-function dopant profiles. However, surface segregation of deposited atoms presents a significant challenge to the application of this process in a variety of materials systems.[1–6] For many semiconductors the substrate temperature required to suppress dopant segregation is too low for high-quality epitaxy.[4,7,8] In some cases, the temperature can be lowered sufficiently without compromising film quality.[5,9] At least for Si(100) MBE, low-temperature epitaxy can proceed for a limited thickness at which point cycling to high temperature is required before continuing growth.[9]

Although surface segregation can result in broadened dopant distributions, a layer of segregating impurities, commonly called ''surfactants,'' can mediate epitaxial growth at temperatures well below those required for similar growth on a bare surface. Impurity overlayers can promote epitaxial growth by changing the arrangement of substrate adatoms, the mobility of deposited atoms, or the energetics of the growth process.[10] Here, we demonstrate a growth process that can achieve As-delta doping of Si using a growth-mediating Pb overlayer. Surface termination of Si(111) with As followed by Si deposition through 1 ML of Pb results in high-quality crystalline films at 350 °C. While the Pb overlayer segregates to the surface during growth without doping the film, the As atoms remain buried at the substrate–film interface with high levels of substitutionality. This is in sharp contrast to the complete segregation of As observed at temperatures required for epitaxy without Pb.[6]

We have previously demonstrated that a Pb overlayer mediates layer-by-layer Si(111) homoepitaxy by a step-flow growth mode.[11] High-quality films have been grown on the As-free Si(111) surface at temperatures as low as 310 °C. Other impurities which have been shown to mediate Si(111) homoepitaxial growth include elements from groups III and V,[6,12] as well as Au (Ref. 13) and Sn.[14] With the important exceptions of Sn and Pb, these impurities are known to be electrically active in Si. Moreover, Sb and Ga overlayers have been shown to be incorporated in films as they mediate growth.[6] In this study the doping and growth-mediating properties of impurities are decoupled by using two species, namely, As and Pb.

We used *n*-type, Si(111) wafers miscut $2.3°\pm0.1°$ towards $[11\bar{2}]$ (resistivity $>1000\ \Omega\,cm$). Each sample was degassed at 500 °C, heated to 850 °C to remove the oxide, and cooled at a maximum rate of 1 °C/s. Arsenic termination was achieved by heating the sample to 800 °C and then slowly cooling in the presence of arsenic vapor at a pressure of 1×10^{-6} Torr. The 1×1 low-energy electron diffraction (LEED) pattern and *in situ* Rutherford backscattering spectrometry (RBS), giving a coverage of 7.3×10^{14} cm^{-2} As atoms, are consistent with As on substitutional sites on the surface.[15]

As in the case of Pb-mediated homoepitaxy on the As-free Si(111) surface,[11] a Pb coverage of 1 ML ($1\ ML=7.83\times10^{14}\ cm^{-2}$) must be maintained during growth on As-terminated Si(111) in order to achieve high-quality films. In both cases Pb is codeposited with Si during growth due to significant Pb desorption at the growth temperature of 350 °C. However, the desorption rate of submonolayer quantities of Pb from As-terminated Si(111) is significantly higher than that from the As-free surface.

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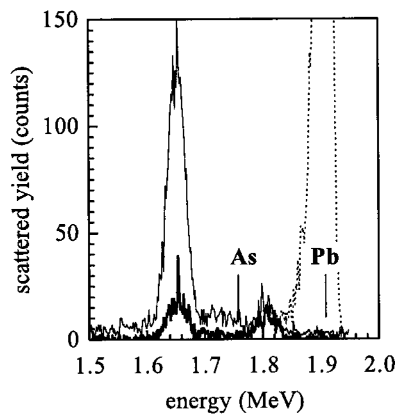

FIG. 1. RBS spectra in the energy range where ions scattered from As atoms in the film are detected. The increase in the scattered yield due to a change in the beam from channeled (thick solid line) to random incidence (thin solid line) demonstrates that most As atoms reside on substitutional lattice sites. The scattered yield from 1 ML of Pb at the surface prior to the HCl treatment is indicated by the dashed line. The energies corresponding to ions scattered from surface As and Pb are indicated.

Therefore, prior to Si deposition, we evaporate 1 ML of Pb onto the As-terminated substrate at 240 °C, a substrate temperature low enough to minimize Pb desorption. Silicon deposition rates were varied between 10 and 30 Å/min. Achieving a steady-state 1 ML coverage of Pb required a Pb flux of 0.25 ML/min at 350 °C. Silicon films up to 1000 Å in thickness have been grown with no sign of decreasing quality with increasing thickness.

Samples were characterized after growth by *ex situ* RBS using 2 MeV $^4He^+$ ions with the incident beam channeled along [111] or in a random incidence with respect to the substrate. The random and channeled ion spectra for a film grown with 1.0 ML Pb are displayed in Fig. 1. Hydrochloric acid was used to remove the Pb layer from the surface. The peak at 1.8 MeV arises from a small quantity of Pb (2.4×10^{13} cm^{-2}) trapped at the substrate–film interface. Pb trapped at the substrate–film interface was also observed in Pb-mediated homoepitaxial growth on As-free surfaces.[11] A 900-Å-thick film grown under As-free conditions was found to have a room-temperature electron sheet concentration in the range of 10^{11} cm^{-2}, approximately two orders of magnitude lower than the concentration of trapped Pb.[16]

The As concentration in the film can be determined from the random incidence spectrum in Fig. 1. The equivalent of 1.04×10^{15} cm^{-2} As atoms is trapped in the film. This value is higher than would be expected from the incorporation of only the As monolayer on the initial substrate surface. The additional As content, 3.1×10^{14} cm^{-2} distributed throughout the film, is due to a background flux from As-contaminated elements inside the growth chamber.[19] The As background in the film is strictly an experimental limitation which can be addressed through practical measures in chamber design and process optimization. The most prominent feature of the As distribution is a peak at 1.65 MeV. The peak position is shifted from the energy of ions scattered by surface As atoms, 1.76 MeV, by an amount corresponding to the energy loss through the 650-Å-thick Si film. This demonstrates that the As layer remains buried at the substrate–film interface. Detector resolution and energy straggle limit the depth resolution with which the As distribution at the substrate–film interface can be determined by the RBS measurements.

The apparent concentration of As atoms in the ion channeling spectrum is the equivalent of 1.7×10^{14} cm^{-2}. The ratio of the apparent concentration to the total concentration from the random incidence spectrum defines the minimum yield associated with the As atoms, χ_{As}. The fraction of substitutional As atoms can be estimated from χ_{As} using the expression $(1-\chi_{As})/(1-\chi_{Si})$.[17] The minimum yield associated with Si atoms, χ_{Si}, is the ratio of the scattered yield behind the Si surface peak for the incident beam in a channeled direction to the yield for random incidence. For the grown sample χ_{Si} is 2.1%±0.3%, a value also obtained for the Si(111) substrate, reflecting the high quality of the film. From Fig. 1 the corresponding value of χ_{As} is equal to 17%, indicating that 85% of the As atoms are on substitutional lattice sites. This estimate represents a lower limit for the substitutional fraction since ion-beam-induced displacement of As atoms during RBS measurements may result in a higher minimum yield χ_{As}.[18]

The spectra presented in Fig. 1 capture the remarkable difference in the behavior between the As and Pb layers. Each As atom of the As-terminated Si(111) surface is bound to three Si atoms and must overcome an activation barrier of 4.0 eV to be removed from the surface.[19] In the absence of reactive surface species, these tightly bound As atoms are essentially immobile at the growth temperature of 350 °C. Indeed, the deposition and complete desorption of monolayer quantities of Pb leave the As-terminated surface intact. Calculations by Kaxiras (Ref. 20) support the experimental finding that a monolayer of As on the Si(111) surface is ineffective as a surfactant.[6] We find that Si films deposited without Pb at 350 °C on As-terminated Si(111) are amorphous after the initial growth of a thin, highly defective layer. In contrast, the activation energy for the desorption of a Pb atom on the Si(111) surface, whether As terminated or As free, is only 0.3 eV for a Pb coverage of 1 ML.[21] In addition, Pb diffusion on the Si(111) 7×7 surface has been observed at temperatures as low as 25 °C.[22] These observations, in conjunction with the negligible solubility of Pb in Si, are strong evidence that the growth conditions favor the surface segregation of Pb and not As.

The high density of As in the delta-doped region enables the detection of As atoms in the Si lattice using a scanning transmission electron microscope in the Z-contrast mode.[23] Image contrast arises from electrons that are scattered to high angles, where the differential scattering cross section approaches the square of the atomic number Z. Figure 2 is a Z-contrast image in a ⟨110⟩ projection. The rows of spots perpendicular to the [111] growth direction arise from the diamond-structure double layers. The spacing of these double layers in Si is 3.13 Å. The bright band of several double layers corresponds to a region in which the As concentration is greater than the minimum detectable concentration of about 2×10^{20} cm^{-3}.[24]

Figure 3 presents a line profile across the substrate–film interface of simultaneously recorded Z-contrast and As K-edge x-ray fluorescence signals. Both measurements yield a full width at half maximum (FWHM) less than 30 Å for the distribution of As at the interface. The As concentration

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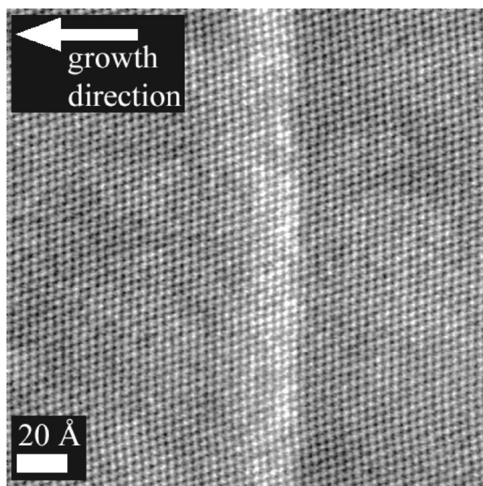

FIG. 2. *Z*-contrast image of an As delta-doped region (⟨110⟩ projection).

along the line profile has been calculated using the ratio of the As–K and Si–K edge intensities. The total As concentration in the peak corresponds within measurement error to the initial As coverage of 0.93 ML associated with the As-terminated Si(111) substrate. Secondary ion mass spectrometry of high-quality films confirms that close to a monolayer of As is trapped within a few nanometers of the substrate–film interface. Images of the sample analyzed in Fig. 1 show peaks of similar width in the Z-contrast intensity.

The electrical activity of As has been studied by Hall-effect measurements. With a Hall factor of 1 for degenerately doped n-type Si,[25] the measured electron sheet concentration, n_{Hall}, at 5 K is equal to $8.5\times10^{14}\ \mathrm{cm}^{-2}$ for the sample analyzed in Fig. 1. Comparison of this value with the concentration of As atoms in the film shows at least 83% of all As atoms to be electrically active.

Because the electrical properties of our samples effectively arise from two doped layers, the doped film and the heavily doped interface, n_{Hall} represents a weighted average: $n_{\mathrm{Hall}}=(n_{\mathrm{film}}\mu_{\mathrm{film}}+n_{\mathrm{delta}}\mu_{\mathrm{delta}})^2/(n_{\mathrm{film}}\mu_{\mathrm{film}}{}^2+n_{\mathrm{delta}}\mu_{\mathrm{delta}}{}^2)$, where $n_{\mathrm{film}}(\mu_{\mathrm{film}})$ and $n_{\mathrm{delta}}(\mu_{\mathrm{delta}})$ are the electron sheet concentration (mobility) in the film and in the delta-doped interface, respectively.[26] Therefore, n_{Hall} is less than or equal to the sum $n_{\mathrm{film}}+n_{\mathrm{delta}}$. Hall-effect measurements of films not containing the delta-doped region exhibit an As electrical activity of 85%.[16] With the assumptions that all background As atoms are electrically active (i.e., $n_{\mathrm{film}}=3.1\times10^{14}\ \mathrm{cm}^{-2}$) and that the width of the heavily doped interface is 30 Å, the three-dimensional concentration of electrically active As at the interface region is in excess of $1.8\times10^{21}\ \mathrm{cm}^{-3}$, the highest achieved in a delta-doped layer to date.[27]

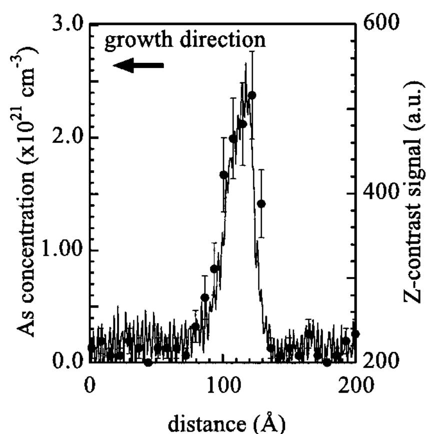

FIG. 3. Line profile on which *Z*-contrast (solid line, right-hand axis) and As *K*-edge x-ray fluorescence (data points, left-hand axis) signals were simultaneously collected. The FWHMs for the *Z*-contrast and x-ray fluorescence signals are 23 and 30 Å, respectively.

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