LOW-TEMPERATURE Si (111) HOMOEPITAXY AND DOPING MEDIATED BY A MONOLAYER OF Pb

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ABSTRACT

The codeposition of Pb during Si (111) molecular beam homoepitaxy leads to high-quality crystalline films at temperatures for which films deposited on bare Si (111) are amorphous. Like other growth mediating elements-- commonly called surfactants-- Pb segregates to the film surface. Ion channeling and transmission electron microscopy reveal nearly defect-free epitaxy for a Pb coverage of one monolayer and temperatures as low as 310 °C. We have deposited films up to 1000 Å in thickness with no indication that this is an upper limit for high-quality epitaxy. However, a decrease in the Pb coverage during growth by only one tenth of a monolayer leads to highly defective films at these temperatures. The codeposition of both As and Pb results in a striking enhancement of the film quality as well. In this case, while the Pb again segregates to the film surface, the As is incorporated into the film with no apparent segregation. Lead-mediated Si epitaxy on As-terminated Si (111) produces high-quality films in which the As remains buried at the substrate-film interface. These results show Pb-mediated Si (111) homoepitaxy to be a promising strategy for the synthesis of layered structures having abrupt nanoscale dopant profiles.

INTRODUCTION

An overlayer of metal atoms on an otherwise clean semiconductor surface can change the growth mode of deposited films.[1,2] Characteristic features of the deposition of semiconductor films through metal overlayers include the promotion of epitaxial growth at low temperatures and the segregation of the overlayer impurity to the surface of the growing film. For Si (111) homoepitaxy the use of monolayer quantities of Ga,[3] Sb,[3] Au,[4] and Sn[5] has been shown to allow lower deposition temperatures than those necessary for the growth of high-quality films on bare surfaces. Reducing the growth temperature mitigates the effects of dopant diffusion, reaction and evaporation of surface metallizations, and thermal stress. With the exception of Sn, all of the previously studied elements are electrically active impurities in Si. While most of the overlayer atoms segregate to the surface of the growing film, the small fraction that is trapped in the epilayer constitutes a significant dopant concentration which can degrade the electronic quality of the film. Doping by the growth-mediating element has severely limited the application of this deposition process in Si device electronics.

We have reported homoepitaxial growth on Si (111) at temperatures as low 310 °C using a 1 ML (1 ML = 7.83×10^{14} atoms/cm^2) Pb overlayer.[6] Films up to 1000 Å in thickness have been grown with no sign of decreasing quality with increasing thickness. The 310 °C growth temperature represents a reduction of 350 °C in the temperature at which thick, high-quality homoepitaxial Si (111) films may be grown on bare surfaces.[7] As with other overlayer elements, the Pb layer segregates from the growing crystal to stay at the surface. Without Pb, epitaxial growth at these temperatures breaks down within a few nanometers of the substrate–film interface, resulting in an amorphous film.

Because of its negligible solubility and isoelectronic character in Si, Pb is an ideal overlayer element for the synthesis of films that are doped via the introduction of a dopant

species during growth. We present the first results for the doping of Si films by the shallow donor As during Pb-mediated epitaxy.

EXPERIMENT

We used *n*-type wafers miscut 2.3 ±0.1° towards [$11\bar{2}$] (resistivity>1000 Ω-cm). The 500 μm-thick Si (111) wafers were cleaved into 1 cmx2 cm samples, chemically oxidized by the Shiraki process, and loaded into an ultrahigh vacuum growth chamber with a base pressure of $1x10^{-10}$ Torr. With the use of direct-current resistive heating, each sample was degassed and then heated to 850 °C to remove the oxide, and cooled at a maximum rate of 1 °C/s to the growth temperature. Sample temperatures were measured with an optical pyrometer, calibrated to the resistance of a sample that displayed intrinsic variation of the carrier concentration with temperature above 150 °C. The resistance of the intrinsic sample was a sensitive function of temperature in the range of interest. All temperatures are accurate to within ±10 °C.

Depositions of Pb and Si were done using an effusion cell and an electron-beam heated rod, respectively. Lead coverages were determined *in situ* to within 5% by Rutherford backscattering spectrometry (RBS). The evaporation sources were masked to produce partially overlapping regions in which Pb and Si were deposited with the intention of simultaneously growing films with and without 1 ML Pb. Imperfections in the masking process, however, yielded a low Pb flux to the area where nominally only Si was to be deposited. We have found that significant desorption of Pb occurs at temperatures above 280 °C.[6] In order to keep the Pb coverage constant during growth of the Si film, Si and Pb were codeposited.

Upon developing a Pb-mediated growth process that yields high-quality films, we introduced an additional effusion cell containing solid As for the study of dopant incorporation during epitaxial growth. Doping of the films was performed by exposing the sample to a flux of As during deposition. A second approach consisted of applying the Pb-mediated growth process to the deposition of Si on As-terminated Si (111). Arsenic termination was achieved by slowly cooling the sample from 800 °C to the deposition temperature of 350 °C in the presence As vapor that resulted in a pressure of $1x10^{-6}$ Torr inside the chamber. The 1x1 low energy electron diffraction (LEED) pattern and *in situ* RBS measurement giving a coverage of $7.3x10^{14}$ cm^{-2} As atoms, or 0.93 ML, are consistent with As on substitutional sites of the Si (111) surface.[8,9] All films involving As doping were deposited at a substrate temperature of 350 °C.

RESULTS

The samples were characterized after growth by *ex situ* 2 MeV $^4He^+$ ion channeling measurements with the incident beam along [111] and the detector aligned in a glancing exit geometry. Figure 1 shows two spectra from a film deposited at 340 °C on a 2.3° miscut substrate. The film grown on a region of the sample with only incidental Pb incorporation shows scattering consistent with a 900 Å layer that is largely amorphous.[6] Films with no Pb contamination also yield spectra characteristic of an amorphous layer. In comparison, the film grown with codeposition to maintain 1 ML Pb during growth shows a dramatic reduction in scattered yield. The minimum yield, χ_{min}, which 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, is 2.4±0.3% for the grown sample. This is identical within measurement error to χ_{min} of 2.2±0.3% measured for a clean Si (111) sample on which 1 ML Pb had been deposited. The area under the peak at 1.9 MeV due to scattering from Pb corresponds to a Pb coverage of 1.08±0.05 ML.

Images and diffraction patterns obtained by cross-sectional transmission electron

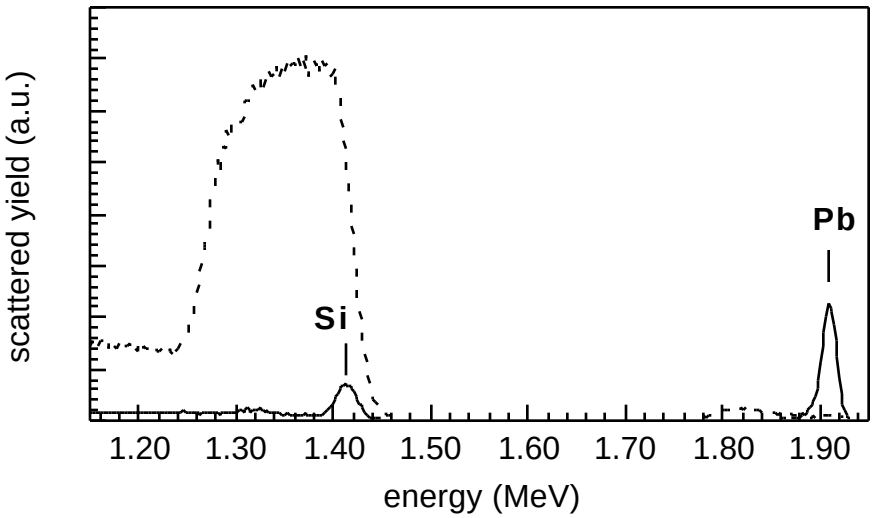

Figure 1. Ion channeling spectra for 900 Å Si films grown on a 2.3° miscut Si (111) substrate at 340 °C with (solid line) and without (dashed line) codeposition to achieve 1 ML steady-state Pb coverage. The improvement in crystal quality with 1 ML of Pb present during growth dramatically reduces the scattered yield from the film. Imperfections in the masking process resulted in approximately 0.3 ML Pb distributed throughout the film for which only Si was to be deposited.

microscopy (TEM) show that films grown with at most incidental Pb are amorphous.[6] In comparison, films grown with 1 ML Pb show high-quality epitaxy. Films of excellent crystalline quality can be grown for substrate temperatures as low as 310 °C. Room temperature Hall effect and electrical resistivity measurements show the crystalline films to be *n*-type with electron concentrations in the range of 10^{16} cm^{-3}. Hall mobilities of approximately 900 cm^2/Vs reflect the high quality of the epilayers. Films grown with codeposition rates giving Pb coverages less than 1 ML are defective. Examination of these films by TEM shows the defects to be stacking faults that nucleate at the substrate–film interface.

Having demonstrated the ability to produce high-quality Si epilayers by Pb-mediated growth, we present preliminary results on doping during growth by codepositing As atoms. Because of its significantly lower tendency to segregate compared to other commonly used overlayer elements,[3,10] As is an ideal candidate for forced incorporation by Pb-mediated growth. In Figure 2 the channeled spectrum of an As-containing epilayer shows that As can be incorporated into the film while the Pb still segregates from the growing film to the surface. From RBS measurements with the $^4He^+$ beam in a random incidence [Figure 2 (b)], the equivalent of $3.4x10^{14}$ cm^{-2} As atoms has been trapped in the film. The concentration of As atoms visible in the channeling spectrum is significantly lower, $4.7x10^{13}$ cm^{-2}. The ratio of this concentration to the As content in the film defines the minimum yield associated with the As atoms, $(\chi_{min})_{As}$, and in this case is equal to 14%. The fraction S of substitutional As atoms can be estimated from $(\chi_{min})_{As}$: $S=(1-(\chi_{min})_{As})/(1-(\chi_{min})_{Si})$. We thereby estimate that 88% of the As atoms are substitutional. The electron sheet concentration is $2.9x10^{14}$ cm^{-2} indicating that about 85% of the As atoms are electrically active in agreement with the calculated substitutional fraction.

The As content of the film depicted in Figure 2 is due to a background flux arising from As-contaminated elements inside the chamber that become hot during film deposition. However,

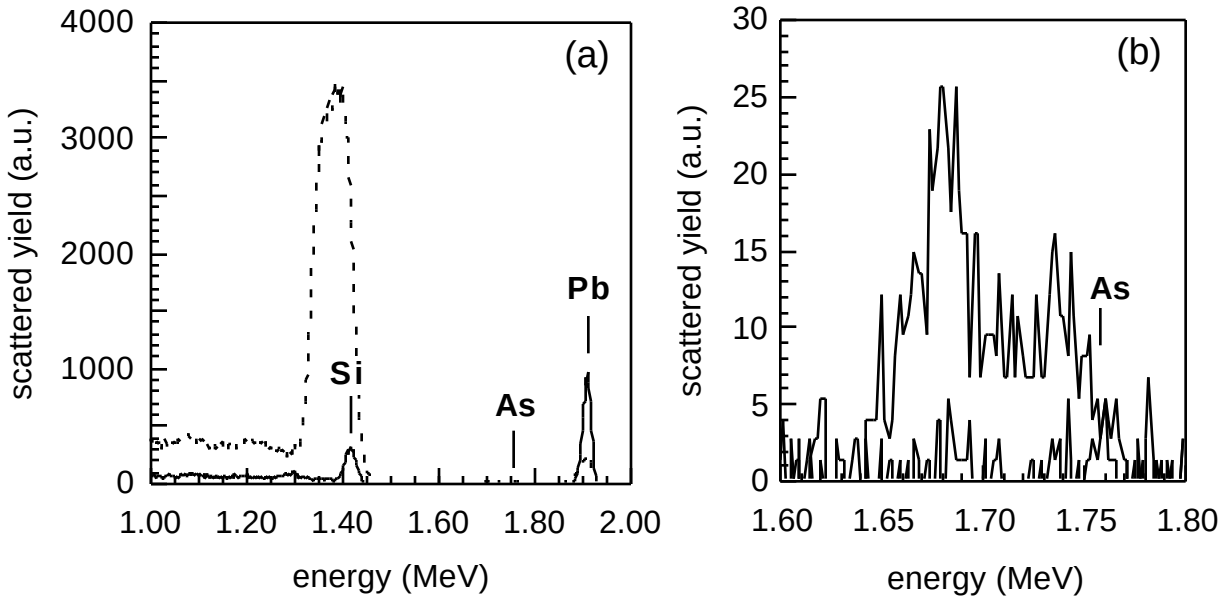

Figure 2. (a) Ion channeling spectra for 600 Å Si films grown on Si (111) at 350 °C in the presence of an As flux with (solid line) and without (dashed line) codeposition to achieve 1 ML steady-state Pb coverage. (b) Ion scattering spectra due to collisions between $^4He^+$ and As atoms in the film. The increase in the scattered yield due to a change in the beam from channeled alignment along [111] (thick solid line) to random incidence (thin solid line) demonstrates that most of the As atoms reside on substitutional lattice positions. The energy corresponding to scattering from surface As is indicated.

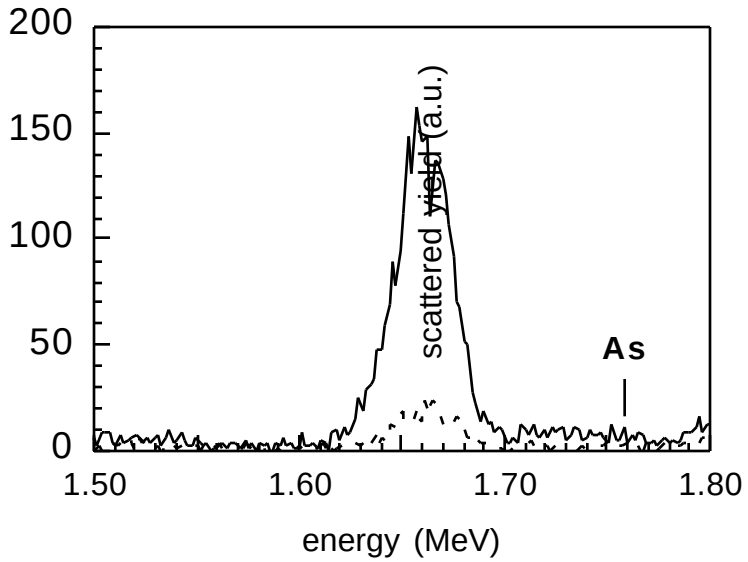

Figure 3. RBS spectrum (solid line) for a film on As-terminated Si (111). The incident beam is in a random orientation with respect to the substrate. The maximum in the scattered yield is due to As trapped near the substrate-film interface. The ion channeling spectrum (dashed line) shows a significant reduction in scattered yield since a large fraction of the As are substitutional. The energy of helium ions that have been scattered from surface As atoms is indicated.

higher As concentrations can be obtained by exposing the substrate directly to the beam of the As effusion cell. We have achieved As concentrations exceeding $6x10^{20}$ cm^{-3} with at least 70% of the As atoms occupying substitutional positions. There is no indication that this is an upper limit to the concentration of As atoms that can be incorporated during Pb-mediated growth.

We have grown Pb-mediated films on initially As-terminated Si (111) substrates. RBS and ion channeling measurements have been performed on these samples. As in the case of Pb-mediated epitaxy on the clean Si (111) surface, high-quality films result. The film associated with the RBS spectrum in Figure 3 contains the equivalent of $9.7x10^{14}$ cm^{-2} As atoms with over 80% occupying substitutional positions. The As that was initially present on the Si substrate remains buried near the substrate-film interface demonstrating that As does not segregate during the Pb-mediated growth process. Efforts to determine the distribution of As atoms are under way.

CONCLUSIONS

One monolayer of Pb on the Si(111) surface during molecular beam homoepitaxy results in the growth of high-quality crystalline films at substrate temperatures well below those required for growth on bare Si (111). We have shown that the codeposition of As and Pb in Si(111) MBE yields high-quality doped films in which the Pb has segregated to the film surface while As has been incorporated into the film. At least 70% of the As atoms both are positioned at substitutional lattice positions and are electrically active. The codeposition of Pb during growth on an initially As-terminated Si (111) surface also results in high-quality crystalline films, the As remaining buried at the substrate-film interface. These results show Pb-mediated Si (111) homoepitaxy to be a promising strategy for the synthesis of layered structures having abrupt nanoscale dopant profiles.

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