

Low-temperature Si molecular beam epitaxy: Solution to the doping problem

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(Received 2 May 1990; accepted for publication 18 September 1990)

A major problem in group IV molecular beam epitaxy (MBE) is the difficulty to incorporate and control dopants due to the low incorporation probability and strong segregation in Si at typical growth temperatures. It is demonstrated here that growth at low temperatures yields a solution to this doping problem making thermal, coevaporative doping with excellent control possible in Si MBE without the need for any post-growth annealing. Unity incorporation and activation of Sb with concentrations reaching $5 \times 10^{19} \text{ cm}^{-3}$ are achieved for epitaxial growth of Si on Si(100) at temperatures of 325 °C. Hall electron mobilities in the films are close to bulk values indicating the high quality of the films. Capacitance-voltage measurements on Sb δ -doped films have full widths at half maximum of $\lesssim 50 \text{ \AA}$, the narrowest Sb-doping profiles in Si determined with an electrical technique.

One of the major problems in group IV molecular beam epitaxy (MBE), significantly impeding its applications to devices, is the incorporation and control of dopants, customarily referred to as the "Si doping problem."¹ Unlike dopant incorporation in III-V compounds, where thermal, coevaporative doping gives excellent results, doping in Si at typical growth temperatures is dominated by low incorporation probabilities and segregation.²⁻⁶ This is particularly true for the common dopants Ga, In, and Sb. The *p*-type dopant B exhibits similar problems, although to a smaller extent.⁷ A variety of methods has been introduced to overcome this deficiency, such as low-energy ion implantation,⁸ solid phase epitaxy (SPE),⁹ secondary-ion implantation (potential enhanced doping),¹⁰ high-temperature deposition,^{2,4} buildup and flash-off techniques,¹¹ and use of a special electrostatic electron beam evaporator.^{12,13} Nevertheless, these methods introduce new difficulties, such as defect formation, temperature-, growth-rate-, and species-dependent incorporation, complicated growth schedules and equipment, sensitivity to small variations in process parameters, or solid-state diffusion.

Lowering the growth temperature to a value where segregation is completely suppressed obviously constitutes one approach to a solution of the doping problem. It can be inferred from Jorke's model of segregation and incorporation of Sb in Si(100) that this regime is entered at growth temperatures significantly below 400 °C.³ On the other hand, it is usually assumed that for growth of a film with a finite thickness in finite time there is a temperature, T_{epi} , separating the regime of epitaxial, single crystalline growth of the film from the regime of amorphous or polycrystalline growth.¹⁴ While values for T_{epi} vary in the literature,¹⁵ it is generally accepted that growth of Si on Si(100) in MBE requires growth temperatures of at least 400–450 °C.¹³ This is *above* the temperature to suppress segregation. However, it has been shown recently that the concept of an epitaxial temperature is not appropriate. Instead growth at a given temperature always proceeds epitaxially for a certain limiting thickness, h_{epi} , before the film be-

comes amorphous.¹⁶ This thickness falls off exponentially with decreasing temperature following an Arrhenius relation with a growth-rate-dependent activation energy. This exponential dependence has qualitatively been predicted in a recent theoretical model.¹⁷ For a growth rate of 0.2 Å/s we find an activation energy of 0.2 eV and a pre-exponential of $7 \times 10^4 \text{ \AA}$, i.e., at 325 °C $h_{\text{epi}} \approx 1500 \text{ \AA}$. Growth of epitaxial layers of thickness $n \times h_{\text{epi}}$ is accomplished by interrupting growth and annealing the sample at 500 °C for 100 s every h_{epi} .¹⁶ Thus a finite thickness can be grown at any temperature and in particular epitaxial growth of significant thickness even at room temperature has been demonstrated.¹⁶ Since segregation and low incorporation can be avoided at growth temperatures below $\approx 400 \text{ °C}$, the feasibility of low-temperature growth results in a solution to the doping problem.

Unity incorporation of thermal, coevaporated dopants has been achieved previously using room-temperature deposition (SPE).⁹ The resulting films are amorphous and are recrystallized using post-growth annealing. Of course for technologically interesting films, the dopants need not only be incorporated, but also be electrically active. Complete activation in SPE films is only achieved by annealing at temperatures exceeding 900 °C¹⁸ or high-temperature annealing of the dopant before SPE growth of the Si.¹⁹ Both approaches are not compatible with structures such as strained layers and doping superlattices where strain relief and bulk diffusion are of concern.

We show here that a solution to both problems, the segregation and low incorporation of conventional high-temperature MBE films and the low electrical quality of conventional SPE films, does exist. We demonstrate that unity activation up to dopant concentrations of $5 \times 10^{19} \text{ cm}^{-3}$ at a growth temperature of 325 °C is possible *without* the need for any post-growth processing. We will demonstrate the sharpness of the doping distributions by reporting *CV* measurements on Sb δ -doped layers. We will discuss Sb as dopant, since it is the most difficult *n*-type dopant in Si with regard to incorporation and segregation,

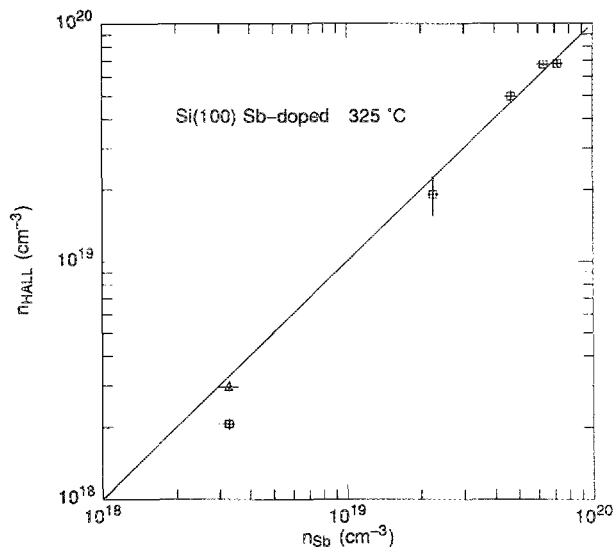


FIG. 1. Hall concentration of n -type carriers in 500-Å-thick Sb-doped films (squares), measured in the van der Pauw geometry at room temperature, as a function of atomic concentration measured by SIMS and ion scattering. The triangle at the lowest measured concentration is obtained after correction for the surface depletion width; this effect is negligible at the higher concentrations. The solid line corresponds to unity activation.

but outstanding with regard to ease of evaporation. However, the results and concepts are not limited to Sb, and apply as well to a p -type dopant such as B.

All samples were grown in a custom-made MBE system of base-pressure 4×10^{-11} Torr. Si was evaporated at rates of 0.2 Å/s from an e -beam evaporator, Sb from a Knudsen cell. Pressure during evaporation was less than 3×10^{-10} Torr, mainly due to hydrogen (85%). Temperatures below 500 °C were determined from an extrapolation of the heating current, calibrated with an infrared pyrometer at temperatures above 500 °C as well as eutectic reactions. While the temperatures around the typical growth temperatures are reproducible to within ± 10 °C, the absolute accuracy is ± 25 °C. Si(100) substrates of nominally zero miscut were chemically cleaned and a protective oxide layer grown as the final step.²⁰ The oxide was desorbed *in situ* by the Si-beam cleaning technique²¹ at a temperature of 800 °C and a Si deposition rate of 1.6×10^{13} cm⁻² s⁻¹ for a total of 15 Å. A Si buffer layer was subsequently grown of thickness ≈ 200 Å.

In Fig. 1 we show the results of Hall measurements on Sb-doped 500-Å-thick films on 1000 Ω cm p -type Si(100) substrates. The Hall concentration is given as a function of Sb concentration, determined by SIMS or Rutherford backscattering. Concentrations up to 5×10^{19} cm⁻³ are measured, which exceed significantly the solid solubility limit of Sb in Si. The solid line indicates 100% activation which is indeed achieved within the experimental uncertainty. Since the surface depletion layer width at a concentration of 3.2×10^{18} cm⁻³ (the film with the lowest concentration measured here) is ≈ 150 Å, depletion introduces a significant reduction of the free-carrier concentration at this low concentration. Correcting for this depletion effect gives the triangle in Fig. 1. All of the sam-

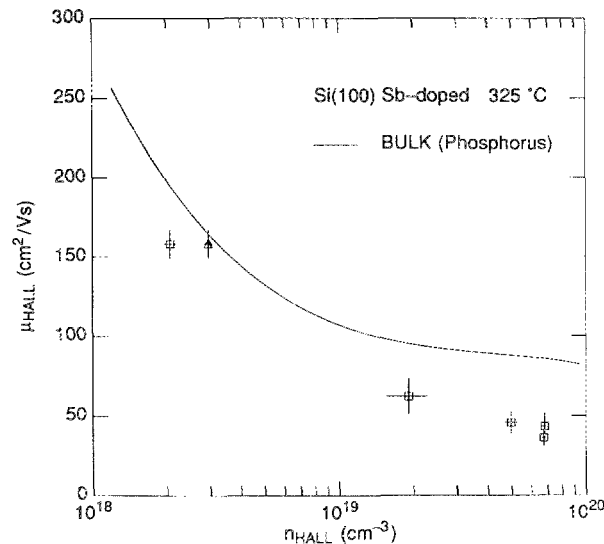


FIG. 2. Hall mobilities for the samples of Fig. 1 as a function of atomic concentration. The solid line represents the bulk mobility of n -type Si doped with phosphorus.

ples significantly exceeded the small activation of 0.23 reported by Jorke *et al.*²² for uniform Sb doping at a concentration of 10^{18} cm⁻³ and a growth temperature of 300 °C.

Hall electron mobilities for the samples of Fig. 1 are shown in Fig. 2 together with the bulk electron mobilities for phosphorus-doped Si (solid line).²³ While the mobility for the film with $\approx 5 \times 10^{18}$ cm⁻³ reaches the value of the bulk reference, higher concentrations show a reduction. Possible causes, such as differences in mobilities for P and Sb dopants, defects in the Si matrix, or defects induced by the very high concentration of Sb, are currently under investigation. The observed unity activation and the reported²⁴ dissociative adsorption of Sb make the existence of Sb₄ complexes in the epitaxial film unlikely.

Several Sb δ -doped Si epitaxial films were grown to assess the spatial localization of the Sb impurities and the relevance of diffusion and segregation effects. The doping spike of density 4×10^{12} cm⁻² was centered in 2000 Å of slightly (nominally 1×10^{16} cm⁻³) n -doped material, grown on 0.01 Ω cm n -type Si(100) substrates. Capacitance-voltage (CV) measurements at 2.0 MHz are used for the profile in Fig. 3. The peak has a full width at half maximum (FWHM) of ≈ 50 Å. It appears at a larger depth probably due to the existence of oxide at the surface. This is the sharpest Sb-doping profile in Si measured by an electrical technique to our knowledge. From CV profiles reported by van Gorkum *et al.*¹⁹ for Sb δ layers grown by SPE we infer a FWHM of ≈ 75 Å for this growth technique at a concentration of 4×10^{12} cm⁻².

Recently, the resolution of the CV technique on δ -doped semiconductors was shown to be limited by the uncertainty principle, i.e., by the spatial extent of the electron wave function.²⁵ For the present parameters a resolution of ≈ 20 Å is calculated, significantly smaller than the experimentally determined value. This difference could be due to some small amount of broadening of the δ layer itself. However, a sufficiently large series resistance in the

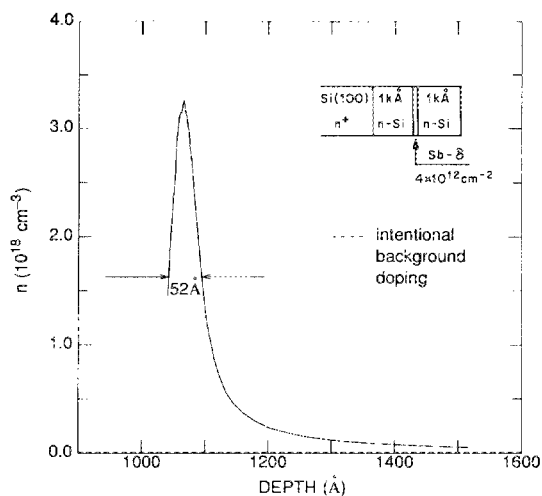


FIG. 3. Capacitance-voltage profile of a Sb δ -doped Si layer with $N_{\text{Sb}}^{\text{D}} = 4 \times 10^{17} \text{ cm}^{-2}$ embedded in 2000 Å lightly ($1 \times 10^{16} \text{ cm}^{-3}$) n -doped Si.

sample has the same effect. At present we cannot discriminate between these two possibilities. Nevertheless, the narrow CV profile demonstrates the successful suppression of segregation and diffusion at the chosen low growth temperature.

In conclusion, we have demonstrated that thermal, co-evaporative doping of Si with a high degree of accuracy and reproducibility and good electrical characteristics is possible at low growth temperatures. Unity incorporation and activation of Sb in Si(100) without any post-growth processing was achieved with concentrations up to $5 \times 10^{19} \text{ cm}^{-3}$, significantly exceeding the solubility limit. Higher concentrations, as well as application of the technique to other dopants, are straightforward. CV measurements on Sb δ -doped layers show the sharpest doping profiles in Sb-doped Si reported with an electrical technique and demonstrate that segregation and diffusion of the Sb dopant are negligible. Hall mobilities close to the values of phosphorus-doped bulk samples indicate the high quality of the films.

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