EFFECTS OF BORON CONCENTRATION ON $\text{Si}_{1-x}\text{Ge}_x$ PROPERTIES FOR INTEGRATED MEMS TECHNOLOGY

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ABSTRACT

The effects of boron (B) concentration on the chemical, electrical, and mechanical properties of p+ polycrystalline germanium (poly-Ge) and p+ polycrystalline silicon-germanium (poly- $\text{Si}_{1-x}\text{Ge}_x$) films are reported. Experimental results show that heavy B doping is beneficial for increasing the deposition and etch rates, as well as for reducing the surface roughness of p+ poly-Ge sacrificial films. However, structural poly- $\text{Si}_{1-x}\text{Ge}_x$ films become more compressive, and show a slight increase in strain gradient, with increasing B content. Analytical models fit to the experimental data for conductivity, residual stress, and strain gradient have been generated as a guide for co-optimization of B and Ge content.

INTRODUCTION

Polycrystalline silicon-germanium (poly- $\text{Si}_{1-x}\text{Ge}_x$) is an attractive material for post-CMOS integration of MEMS with electronics because it can be used to form high-quality structural films with a thermal process budget that is compatible with standard electronics [1-2]. Germanium (Ge) is an attractive sacrificial material because it can be deposited rapidly at low temperatures ($< 350^\circ\text{C}$) and readily etched selectively to metals, Si, SiO_2 , Si_3N_4 , and $\text{Si}_{1-x}\text{Ge}_x$ ($x < 0.7$) in a heated peroxide (H_2O_2) solution [3]. *In-situ* p-type doping is preferred because it provides enhanced deposition rate and lower resistivity [1]. Previous studies of structural poly- $\text{Si}_{1-x}\text{Ge}_x$ layers focused on very heavily boron doped films (B concentration exceeding 10^{20} cm^{-3}) for minimum electrical resistivity ($< 1 \text{ m}\Omega\text{-cm}$) and maximum deposition rate. Recently, however, heavy boron doping was reported to enhance the etch rate of p+ $\text{Si}_{1-x}\text{Ge}_x$ ($x > 0.7$) in H_2O_2 , which compromises the etch selectivity between the p+ Ge sacrificial material and the $\text{Si}_{1-x}\text{Ge}_x$ structural layer(s) during the long etch needed to release the MEMS structures [4].

The effects of boron concentration on the properties of poly-Ge films and poly- $\text{Si}_{1-x}\text{Ge}_x$ films are presented in this paper, which aims to highlight the tradeoffs for process optimization. The B-doping dependence of Ge deposition rate, etch rate, and surface roughness is first discussed. Experimental data are then reported for p+ $\text{Si}_{1-x}\text{Ge}_x$ ($x < 0.7$) films, to show the effects of boron content on residual stress and strain gradient. It should be noted that all of the films studied in this work are suited for post-CMOS processing, since they are deposited at a temperature less than or equal to 425°C with no post-deposition annealing treatment.

EXPERIMENTAL DETAILS

P-type Ge films were deposited at 350°C and 300mT onto oxidized Si wafers, with a very thin ($< 10\text{nm}$ thick) amorphous-Si seed layer, in a conventional low-pressure chemical-vapor deposition (LPCVD) system using GeH_4 (170 sccm) as the Ge precursor gas, and B_2H_6 as the dopant gas. The B_2H_6 is diluted (to 10%) in H_2 and is introduced from the back of the furnace through an injector in order to minimize gas depletion effects, while the GeH_4 is simply introduced through a ring at the front of the tube. Because of this arrangement, the B concentration and Ge content are dependent on wafer position inside the tube (Fig. 1). The B concentration in each of the deposited films was determined by Secondary Ion Mass Spectrometer (SIMS) analysis. The sheet resistance of the films was measured at several points on each wafer using a four-point probe instrument; average values are reported herein. The Ge films were patterned into test structures using conventional optical lithography and reactive ion etching (RIE) using Cl_2/HBr chemistries. The film thickness was then determined from step-height measurements using a Dektak surface profilometer. The Ge etch rate in a 90°C H_2O_2 solution was then characterized by monitoring the step height in-between etch treatments, for films of various Ge contents.

P-type poly- $\text{Si}_{1-x}\text{Ge}_x$ films were deposited at 425°C and 400mT in the same LPCVD system, onto oxidized Si wafers (p-type, 1 ohm/square) coated with $\sim 2.2\mu\text{m}$ of undoped low temperature oxide (LTO). SiH_4 was used as the precursor Si gas (Fig. 1). The B concentration and Ge content in the deposited films were determined by SIMS analysis (2.5% accuracy), and varied from $1 \times 10^{19} \text{ cm}^{-3}$ to $5 \times 10^{21} \text{ cm}^{-3}$ and 61% to 67%, respectively. In order to determine thin film stress, wafer curvature measurements were made using a Tencor FLX-2320 instrument before and after $\text{Si}_{1-x}\text{Ge}_x$ deposition (with the backside $\text{Si}_{1-x}\text{Ge}_x$ film removed). The films were patterned into cantilever-beam test structures (Fig. 2) and then released using a timed etch in 49% concentrated HF. Then, a Veeco Instruments WYKO interferometer was used to measure the tip deflection of $100\mu\text{m}$ - and $50\mu\text{m}$ -long beams to determine the strain gradient.

Figure 1: Schematic Diagram of LPCVD furnace that was used to deposit p+ sacrificial Ge and p+ structural $\text{Si}_{1-x}\text{Ge}_x$ films.

Figure 2: (a) Schematic cross-section and (b) SEM micrograph of cantilever beams that were used to determine the strain gradient of the structural p^+ poly- $\text{Si}_{1-x}\text{Ge}_x$ films.

RESULTS AND DISCUSSION

A. Effect of Boron Doping on Sacrificial Ge Properties

Ideally, a sacrificial material is deposited at a high rate with minimal surface roughness, and is rapidly and controllably etched selectively to the structural material. Thus, we investigated the deposition rate, etch rate (in a 30% H_2O_2 solution maintained at 90°C), and surface roughness of p^+ Ge films as a function of B concentration ([B]). **Fig. 3** shows that the deposition rate increases with [B], and saturates above $\sim 1.8 \times 10^{21} \text{ cm}^{-3}$ at a deposition rate of $\sim 160 \text{ Å/min}$. The etch rate also increases with [B]. As expected, the resistivity drops with increasing [B] (**Fig. 4**). However, it shows an abrupt increase at $\sim 2 \times 10^{21} \text{ cm}^{-3}$ since that deposition condition leads to an amorphous film. Because of the enhancement in deposition rate that accompanies an increase in [B], the atoms adsorbed on the wafer surface have less time to migrate to the lowest energy crystal sites before the next atoms arrive. Thus, as [B] increases, the degree of disorder in the film increases (average grain size decreases – see **Fig. 6**), until ultimately the film is deposited in amorphous form at very high levels of [B].

Atomic force microscopy (AFM) measurements indicate that the more heavily boron doped Ge films are smoother (**Fig. 5**), which is consistent with their higher deposition rate (resulting in smaller average grain size – see **Fig. 6**). Clearly, high [B] is desirable for increasing process throughput, etch selectivity, and film smoothness for sacrificial Ge films. It is important to note that, although the deposition rate can be substantially increased by increasing the deposition temperature, the film roughness also increases. Thus, it is preferable to keep the p^+ Ge deposition temperature below 400°C .

B. Effect of Boron Doping on Structural $\text{Si}_{1-x}\text{Ge}_x$ Properties

The etch rate of p^+ poly- $\text{Si}_{1-x}\text{Ge}_x$ films in a 30% H_2O_2 solution maintained at 90°C was measured and found to be relatively low (25 Å/min) and independent of B concentration, for

Figure 3: Deposition and etch rates of Ge sacrificial layer as a function of B content. The p^+ Ge films were deposited at $T=350^\circ\text{C}$, $P=300\text{mtorr}$, $\text{GeH}_4=170\text{sscm}$. $\text{B}_2\text{H}_6/\text{H}_2$ flow rate was varied from 0sscm to 60sscm.

Figure 4: Resistivity of p^+ Ge sacrificial layer as a function of B content. The p^+ Ge films were deposited at $T=350^\circ\text{C}$, $P=300\text{mtorr}$, $\text{GeH}_4=170\text{sscm}$. $\text{B}_2\text{H}_6/\text{H}_2$ flow rate was varied from 0sscm to 60sscm.

Figure 5: Surface roughness of Ge sacrificial layer as a function of B content. The p^+ Ge films were deposited at $T=350^\circ\text{C}$, $P=300\text{mtorr}$, $\text{GeH}_4=170\text{sscm}$. $\text{B}_2\text{H}_6/\text{H}_2$ flow rate was varied from 0sscm to 60sscm.

Figure 6: X-TEM of p+ Ge films reported in Fig(s).3, 4 and 5. (a)[B]= $5.3 \times 10^{20} \text{ cm}^{-3}$ (b)[B]= $1.1 \times 10^{21} \text{ cm}^{-3}$ and (c)[B]= $1.8 \times 10^{21} \text{ cm}^{-3}$. Average grain size becomes smaller as B content increases because of the higher deposition rate of heavily doped p+Ge. films.

films with Ge content below 65%. Thus, good etch selectivity between sacrificial p+ Ge and structural $\text{Si}_{1-x}\text{Ge}_x$ can be achieved so long as x does not exceed 0.65. The conductivity of poly- $\text{Si}_{1-x}\text{Ge}_x$ films as a function of B concentration is plotted in Fig. 7, and is seen to improve with increasing [Ge] as well as increasing [B]. This is likely due to improved dopant activation and hole mobility with increasing Ge content [5], due to increased grain size [6].

Using a regression analysis methodology that accounts for all the measured data, the best-fitting surface plots for conductivity, residual stress, and strain gradient as a function of B concentration and Ge content were generated (Fig. 7 and Fig. 8). The fitting confidence is 99.5% for conductivity, 89% for residual stress, and 81% for strain gradient. The average residual stress decreases (*i.e.* the film becomes less compressive) with increasing [Ge], but increases for very high [B] (Fig. 8a). The strain gradient decreases with increasing [Ge] and decreasing [B] (Fig. 8b). Thus, optimization of the boron concentration involves a trade-off between electrical properties (conductivity) and mechanical properties (stress and strain gradient). Electrical and mechanical properties each improve with increasing Ge content. Thus, the Ge content should be maximized at ~65%, so that good etch selectivity of Ge in heated H_2O_2 solution is maintained.

Figure 7: p+ poly- $\text{Si}_{1-x}\text{Ge}_x$ conductivity as a function of Ge and B content. The p+ $\text{Si}_{1-x}\text{Ge}_x$ films were deposited at $T=425^\circ\text{C}$, $P=400\text{mtorr}$. SiH_4 , GeH_4 and B_2H_6 flow rates were varied. In the modeling equation of conductivity ($1/\text{m}\Omega\text{-cm}$), [Ge] is in % of Ge content and [B] is in $\text{atoms}/\text{cm}^3/10^{19}$.

Figure 8: p+ poly- $\text{Si}_{1-x}\text{Ge}_x$ (a) residual stress (b) strain gradient as a function of Ge and B content. The p+ $\text{Si}_{1-x}\text{Ge}_x$ films were deposited at $T=425^\circ\text{C}$, $P=400\text{mtorr}$. SiH_4 , GeH_4 and B_2H_6 flow rates were varied. In the modeling equations of residual stress (MPa) and strain gradient (nm^{-1}), [Ge] is in % of Ge content and [B] is in $\text{atoms}/\text{cm}^3/10^{19}$.

For $[\text{B}]=2.5 \times 10^{20} \text{ cm}^{-3}$, the strain gradient is $1.3 \times 10^{-3} \mu\text{m}^{-1}$, which corresponds to a vertical deflection of $1.7 \mu\text{m}$ at the tip of a $100 \mu\text{m}$ -long, $0.8 \mu\text{m}$ -thick cantilever beam. Although this is too high for inertial MEMS device applications (*e.g.* accelerometers and gyroscopes), it may be acceptable for nanoscale MEMS devices such as RF filters. Approaches to reducing the strain gradient include the use of a bi-layer [7] and the use of pulsed excimer-laser annealing (ELA) [8]. Based on the best-fit analytical models, the optimal B concentration for a low resistivity poly- $\text{Si}_{0.42}\text{Ge}_{0.58}$ film is $\sim 5.1 \times 10^{20} \text{ cm}^{-3}$ to achieve minimal residual stress ($\sim 0.0012 \text{ MPa}$) and strain gradient ($\sim 3.75 \times 10^{-3} \mu\text{m}^{-1}$). However, it is important to note this optimal point is an approximation since the models are based on relatively few data points.

Hall measurements were performed to compare the dopant activation level in two p+ $\text{Si}_{0.37}\text{Ge}_{0.63}$ films: Sample A (with $[\text{B}] \cong 4.5 \times 10^{19} \text{ cm}^{-3}$, $\sigma = -22 \text{ MPa}$) and Sample B (with $[\text{B}] \cong 9.7 \times 10^{20} \text{ cm}^{-3}$, $\sigma = -79 \text{ MPa}$). The results are summarized in Table I, and they indicate that all of the B is activated in Sample A, whereas this is not the case for Sample B. Therefore, the fact that the p+ $\text{Si}_{1-x}\text{Ge}_x$ structural films become more compressive at very high B concentrations is likely due to segregation/clustering of boron atoms.

Table I: Hall Effect Measurement Results for p^+ $\text{Si}_{0.37}\text{Ge}_{0.63}$. Sample A ($\sigma = -22$ MPa), Sample B ($\sigma = -79$ MPa)

	Sample A	Sample B
Boron Concentration	$4.5 \times 10^{19} \text{ cm}^{-3}$	$9.7 \times 10^{20} \text{ cm}^{-3}$
Carrier Concentration	$4.5 \times 10^{19} \text{ cm}^{-3}$	$5.1 \times 10^{20} \text{ cm}^{-3}$

Due to the large strain gradient which causes the released structures to bend up (out of plane), it was not possible to operate the fabricated comb-drive test structures in order to obtain measurements of the mechanical quality factor (Q) for this study. Q values of $\sim 20,000$ at 19 kHz resonant frequency have previously been reported for very heavily doped ($\sim [\text{B}] > 6 \times 10^{20} \text{ cm}^{-3}$) poly- $\text{Si}_{0.38}\text{Ge}_{0.62}$ films [9]. The Q was found to increase with post-deposition annealing (RTA) temperature. To investigate possible causes for this change, we annealed similarly doped poly- $\text{Si}_{0.38}\text{Ge}_{0.62}$ films for 1 minute in N_2 at various temperatures (450°C to 600°C) and then performed Hall measurements as well as X-ray diffraction (XRD) analyses. The Hall measurement results did not indicate a significant increase in dopant activation with annealing, which would suggest that excess (non-ionized) B atoms remain. The XRD analysis results show that the as-deposited film has weak (111) texture, which changes to a strong (110) texture after a rapid thermal annealing treatment. The diffraction peaks for the annealed films were significantly larger and narrower, indicating a larger average grain size, as well. Thus, it seems that the improvement in Q with annealing is attributable to improved microstructure, rather than a reduction in segregated B atoms.

C. Ge and B Quantification by SIMS

Since SIMS was used in this work to quantify the concentrations of B and Ge atoms in the $\text{Si}_{1-x}\text{Ge}_x$ films, it is appropriate to highlight here some of the limitations of this characterization technique. SIMS is based on the linear relation between the concentration of the element of interest and its secondary ion yield in a given matrix. It was shown that correctly chosen analytical conditions and quantification techniques allowed SIMS analysis to generate highly accurate and precise data for B implants into $\text{Si}_{1-x}\text{Ge}_x$ structures for bipolar applications [10]. SiGe bipolar structures are typically characterized by relatively small contents of Ge, up to 10-15 atomic percent. On the other hand, CVD layers for MEMS applications require very high Ge contents, typically 60-70%. The ability to perform highly accurate quantification of doping elements in high Ge content $\text{Si}_{1-x}\text{Ge}_x$ films is a major challenge for SIMS. In the current study, quantification of Si and Ge was done with a $\text{Si}_{0.4}\text{Ge}_{0.6}$ epitaxially grown standard and the so-called “missing Si” approach. SIMS measurements were performed on Cameca 4FE7 secondary ion mass-spectrometer, with 4 keV Cs^+ primary ion beam and negative detection mode (28Si^- , 70Ge^- , $11\text{B}28\text{Si}^-$, $11\text{B}70\text{Ge}^-$). The measurement uncertainty achieved in the current study was 2.5% atomic concentration and was assessed by performing SIMS measurements on identical samples.

CONCLUSION

In-situ B doping is beneficial for improving the deposition and etch rate, as well as the surface smoothness, of LPCVD p^+ Ge sacrificial films. Heavy B doping does not increase the etch rate of poly- $\text{Si}_{1-x}\text{Ge}_x$ structural films in heated H_2O_2

solution, as long as the Ge content is below 65%, so that high etch selectivity can be maintained for a Ge sacrificial material. Increasing the B concentration is beneficial for decreasing electrical resistivity, but results in more compressive stress at very high concentrations, as well as slightly higher strain gradient.

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