Journal of
MATERIALS RESEARCH

On the formation of solid state crystallized intrinsic polycrystalline germanium thin films

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(Received 19 September 1996; accepted 21 April 1997)

A two-step heat treatment process has been employed to crystallize low pressure deposited thin films of amorphous germanium. Large grain *p*-type polycrystalline germanium with a Hall effect hole mobility of greater than 300 cm^2/Vs has been obtained. Films with near intrinsic conductivity, necessary for the construction of practical enhancement-mode insulated-gate thin film transistors, were obtained by introducing phosphorus as a compensating dopant. High Hall effect electron mobility of 245 cm^2/Vs has been measured on the resulting *n*-type polycrystalline germanium thin films.

I. INTRODUCTION

Polycrystalline thin film transistors (TFT's) have been used in a number of important applications. These include three-dimensional stacked transistors for static random-access memories, pixel, and drive transistors for liquid crystal display (LCD) panels, integrated sensors, etc.

In many such applications, low processing temperature is required.[1] In the case of LCD's, the constraint on the processing temperature is quite stringent since the inexpensive glass substrates on which the transistors are formed typically cannot withstand temperature much higher than 550 °C.

Currently, silicon (Si) based amorphous or polycrystalline TFT's are being used, the former typically in the pixel arrays[2] of LCD's. The higher electron and hole mobilities of the latter make it possible to realize also complementary metal-oxide-semiconductor (CMOS) control and driver circuits directly on the inexpensive glass substrates.

The main drawback of the conventional technique of forming the transistor active layers of Si-based polycrystalline TFT's by the pyrolysis of silane (SiH_4) gas in a low pressure chemical vapor deposition (LPCVD) system is the high temperature required, typically around 600 °C. For reduced-temperature processing, polycrystalline alloys of silicon and germanium ($Si_{1-x}Ge_x$) have been extensively studied and reported.[3,4] An added advantage of using $Si_{1-x}Ge_x$ thin films is their higher carrier mobilities than those found in pure Si thin films.

Recently, the use of polycrystalline Ge (polygermanium) thin film as a semiconducting material with the potential to enable even lower processing temperature and provide even higher carrier mobilities has been investigated.[5] The deposition and the characterization of such thin films have been reported. While polygermanium thin films indeed have been obtained at a low deposition temperature of 300 °C, they exhibit high *p*-type conductivity even in the absence of any deliberate doping. This makes it difficult to realize enhancement-mode insulated-gate field effect transistors (IGFET's). Furthermore, it is also desirable to improve the quality of the polygermanium by reducing the density of grain boundaries, the presence of which degrades the electrical performance of the resulting devices. Therefore, the present work is motivated by the need to realize thin films exhibiting "intrinsic" conductivity and the desire to produce large-grain thin films with reduced densities of grain boundaries.

In this work, the technique of counterdoping using implanted phosphorus has been explored for the formation of intrinsic thin films, and the technique of solid phase crystallization of Ge deposited in the amorphous state has been explored for the formation of large-grain polygermanium films. The latter technique has been widely employed to obtain large-grain polycrystalline silicon thin films. The results of the experiments are contained in this report.

II. EXPERIMENTAL

Boron doped (15–25 Ω-cm), (100) oriented, 525 μm thick Si wafers with diameters of 100 mm were used as the starting substrates. The wafers were first thermally oxidized in a dry oxygen ambient at 1000 °C in a Thermco TMX 9001 oxidation furnace. The thickness of the resulting oxide was about 100 nm. The wafers were subsequently transferred to a Thermco TMX 9001 LPCVD furnace for the thin film deposition and the subsequent heat treatments.

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Since it was difficult to induce Ge deposition on thermally grown silicon dioxide, a thin layer of amorphous Si "nucleation" layer was first deposited. The temperature, the pressure, and the SiH_4 gas flow rate for the deposition of the Si layer were, respectively, 500 °C, 300 mTorr, and 150 sccm. Typically, a thickness of approximately 20 nm was obtained for a deposition time of 15 min. Subsequent to the amorphous silicon deposition, amorphous germanium was deposited. Typical deposition temperature, pressure, and germane (GeH_4) gas flow rate were, respectively, 300 °C, 600 mTorr, and 45 sccm. Thermal treatment was done in the same furnace at a pressure of 300 mTorr in pure N_2.

Summarized in Table I are the different conditions for the deposition of and the heat treatments received by the amorphous Ge thin films.

III. CRYSTALLIZATION OF AMORPHOUS GERMANIUM

A representative x-ray diffraction (XRD) spectrum of the as-deposited films is shown in inset A of Fig. 1. None of the commonly observed {111}, {220}, and {311} Ge peaks is present. This is a strong indication that the as-deposited films are amorphous.

The metastable amorphous state converts to the polycrystalline state when subjected to appropriate heat treatments. This is evident from the XRD spectrum shown in inset B of Fig. 1, typical of those obtained from samples after 20 h of heat treatment at 350 °C. Peaks corresponding to the {111}, {220}, and {311} orientations can be seen, but the existence of a broad low-intensity spectrum around the {111} peak indicates that a fraction of the film is still amorphous and that the crystallization is not complete. It is estimated from the widths of the diffraction peaks that the average size of the grains is between 150 nm and 300 nm. The sheet resistance at this point is greater than $10^5\ \Omega/\square$. After an additional heat treatment of 500 °C for 30 min, crystallization is essentially complete, as indicated by the disappearance of the broad low-intensity spectrum around the {111} peak in the XRD spectrum shown in the main body of Fig. 1. After this second heat treatment at 500 °C, the average size of the {111} grains is about 450 nm, the sheet resistance drops to about $2 \times 10^3\ \Omega/\square$, and

TABLE I. Conditions of the deposition of and the thermal treatment received by the amorphous germanium thin film.

	Deposition: 600 mTorr 300 °C, GeH_4 = 45 sccm		Annealing: 300 mTorr N_2	
Sample	Deposition time (min)	Thickness (nm)	First annealing at 350 °C	Second annealing at 500 °C
029, 030N, 0181	300	303	20 h	1h
018C	90	150	20 h	. . .
026, 027N, 0171	200	201	. . .	1 h
A, B, ..., H	60	60	20 h	1 h

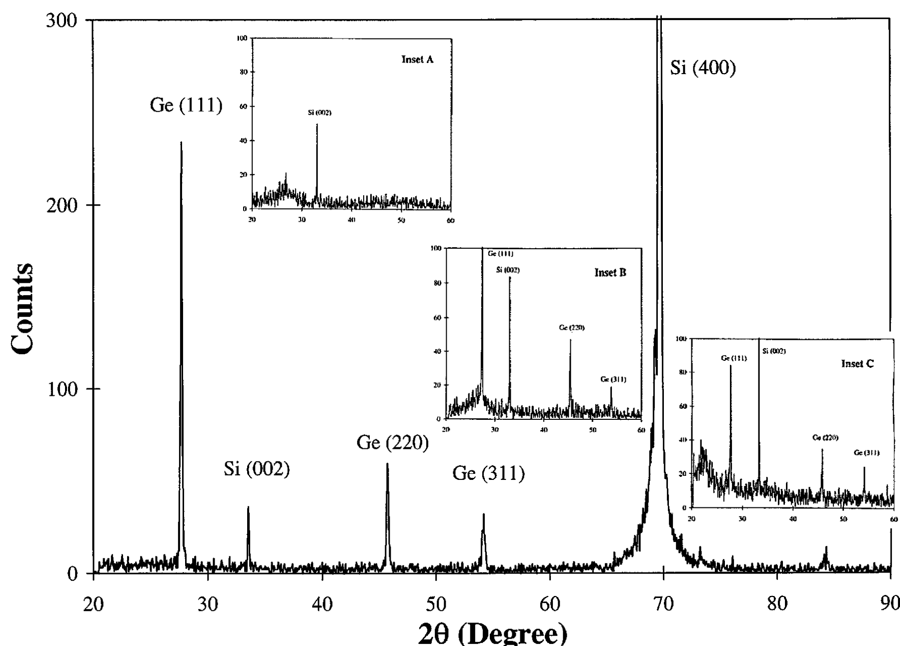

FIG. 1. Typical x-ray diffraction spectrum of a germanium thin film after a two-step crystallization heat treatment: first at 350 °C for 20 h and then at 500 °C for 1 h. Inset A: As-deposited. Inset B: Single-step crystallization: 350 °C for 20 h. Inset C: Single-step crystallization: 500 °C for 30 min.

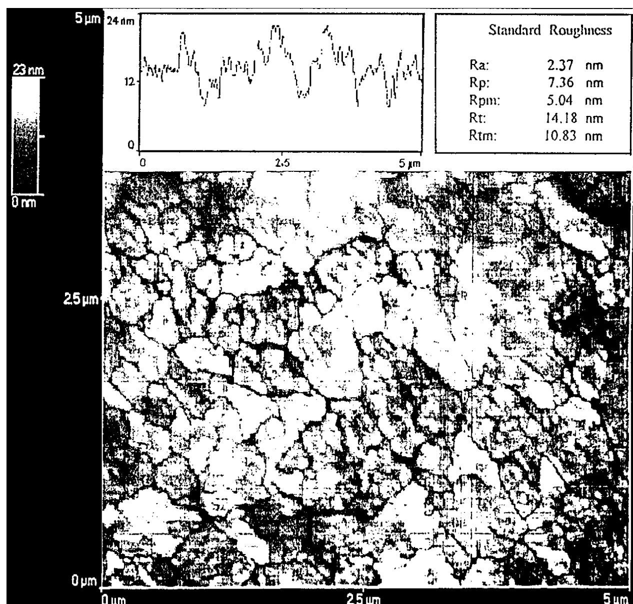

FIG. 2. Atomic force microscope scan showing the surface roughness of polygermanium after the two-step heat treatment.

the Hall effect mobility is above 300 cm^2/Vs. This value, though a factor 10 less than that of bulk Ge, is already good enough for LCD driver circuits. The average surface roughness of polygermanium is about 2.4 nm (Fig. 2), comparable to films deposited in the polycrystalline state.

The effectiveness of a single heat treatment at 500 °C for 30 min was investigated. Crystallization was almost complete, as indicated by the XRD spectrum shown in inset C of Fig. 1, but the average grain size is smaller (8 nm to 168 nm) and the quality of the resulting films is not as good. A smaller Hall effect mobility of only about 180 cm^2/Vs was measured. No improvement in the mobility was observed even after the duration of the heat treatment was extended to 2 h.

It is well known from classical nucleation theory that, when plotted against temperature, the steady state nucleation rate exhibits a bell-shaped curve[6] which goes through a maximum at a certain intermediate temperature (T_m). If the crystallization were performed at a temperature below T_m, then the nucleation rate would decrease with reducing temperature. When the two single-step crystallization processes are compared, it can be seen that larger crystal grains are obtained after the 20-h 350 °C heat treatment than after the 30-min 500 °C treatment. This most likely results from a reduced nucleation rate at the lower crystallization temperature. In the two-step crystallization process, the first heat treatment at 350 °C provides a low density of nuclei, and the subsequent treatment at 500 °C speeds up the grain growth and completes the crystallization of the film by consuming the remaining amorphous fraction of the thin film. Therefore, a two-step crystallization schedule with a low temperature nucleation phase followed by a high temperature grain growth phase

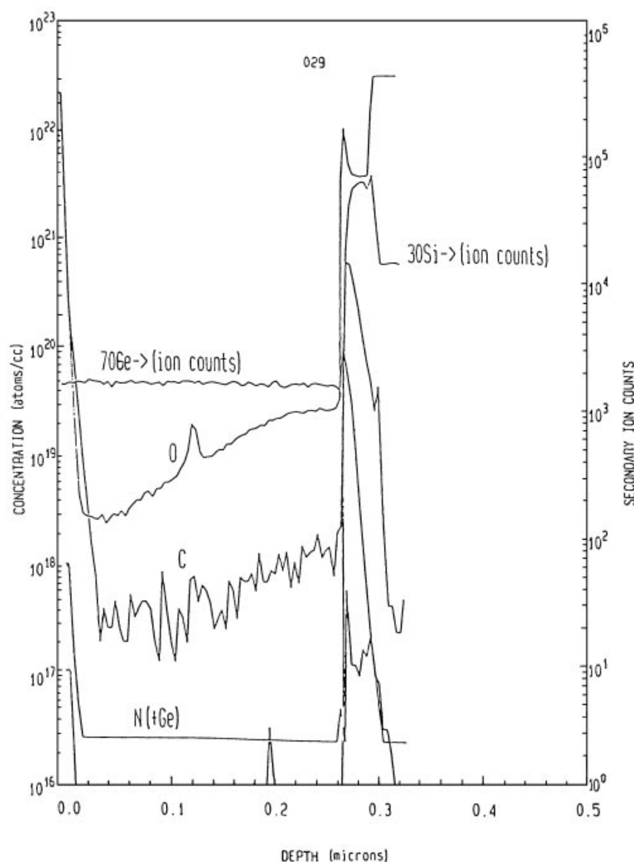

FIG. 3. SIMS depth profiling showing lack of unintentional boron and phosphorus impurities.

produces better quality polygermanium than a single-step high temperature crystallization schedule. This effect is indeed consistent with our observations presented above.

IV. FORMATION OF INTRINSIC THIN FILMS

Whether the polygermanium was deposited in the polycrystalline state or crystallized from the amorphous state, Hall effect measurement showed that it exhibited *p*-type conductivity. This is similar to polycrystalline silicon crystallized from the amorphous state, which has also been shown to exhibit weak *p*-type conductivity.[7] This *p*-type conductivity in polygermanium remained unchanged if the starting substrates were phosphorus instead of boron doped, thus making it unlikely that unintentional dopants were introduced from the substrate. SIMS depth profiling (Fig. 3) also verified that no traces of either boron or phosphorus were detected in the polygermanium thin films. It is proposed that the *p*-type conductivity is caused by localized shallow electronic states located near the edge of the valence band, particularly in the grain boundaries.[8] This lack of intrinsic conductivity makes it difficult to realize low-voltage and low-power enhancement-mode IGFET's.

The use of phosphorus as a compensation dopant to form intrinsic polygermanium was investigated. Samples were initially processed according to the conditions given

TABLE II. Comparison of the electrical parameters of polygermanium before and after the phosphorus compensation. The numbers in the parentheses are the corresponding values before the phosphorus compensation.

	Sample			
	0171	018C	030N	026
Phosphorus compensation	2×10^{13} cm^{-3}, 160 keV	2×10^{13} cm^{-3}, 160 keV	2×10^{13} cm^{-3}, 160 keV	1.2×10^{15} cm^{-3}, 160 keV
Bulk resistivity (Ω-cm)	0.30 (0.05)	0.24 (0.04)	0.22 (0.07)	0.002 (0.05)
Conductivity type	p (p)	p (p)	p (p)	n (p)
Hall effect mobility (cm^2/Vs)	31.4 (135)	59.1 (240)	165 (311)	244 (281)

in Table I, then implanted with singly charged phosphorus ions at an energy of 160 keV and a dose of 2×10^{13} cm^{-2}. Implant activation was performed at 500 °C for 1 h. Relevant electrical parameters before and after the compensation are summarized in Table II. While the Hall effect measurements indicated the films were still p-type, the increase of the resistivities proved clearly that compensation had occurred, independent of the heat treatment schedule before the implantation. When the dose was increased to 1.2×10^{15} cm^{-2}, the Hall coefficient became negative, indicating that the conductivity had turned n-type. The resulting resistivity and Hall effect electron mobility were, respectively, 2.2×10^{-3} Ω-cm and 245 cm^2/Vs. Therefore, it is potentially possible to selectively realize highly conductive n-type gate, source, and drain electrodes at a relatively low processing temperature of 500 °C.

Clearly, conductivity types from p to intrinsic to n should be realizable by controlling the dosage of the phosphorus implantation. This is verified by the experiments involving samples A through H, into which progressively higher phosphorus dosages from 2×10^{13} cm^{-2} to 2×10^{14} cm^{-2} were implanted. Implant activation was again performed at 500 °C for 1 h. A comparison of the sheet resistance before and after the phosphorus compensation is shown in Fig. 4. As the phosphorus dosage is increased, the sheet resistance first increases due to carrier compensation and then drops due to increasing electron concentration. At around 1×10^{14} cm^{-2}, the material is close to intrinsic.

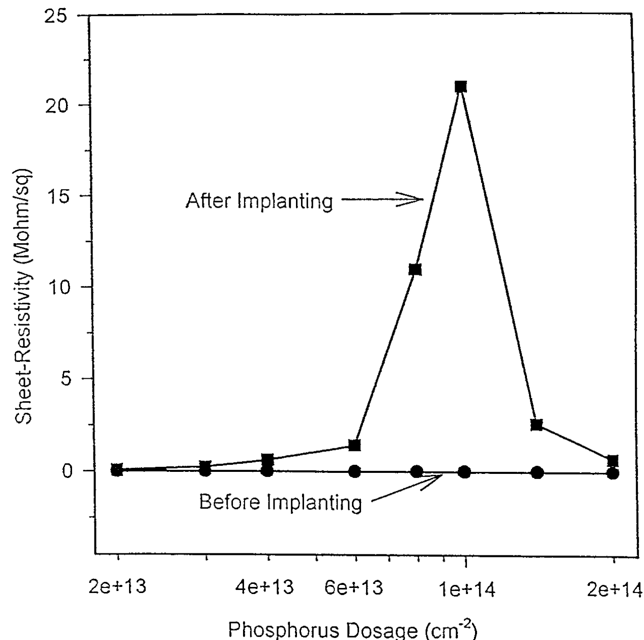

FIG. 4. Dependence of the polygermanium sheet resistance on the dosage of the phosphorus implant. The sheet resistance before the introduction of phosphorus is also given as a reference.

V. CONCLUSION

A two-step crystallization schedule with an extended low temperature (350 °C) heat treatment followed by a short higher temperature (500 °C) treatment has been proposed to produce high quality polygermanium thin films. The conductivity of the polygermanium thin films can be controlled by introducing phosphorus as a compensation dopant. Intrinsic conductivity required for the formation of enhancement-mode IGFET's can be easily obtained by suitably adjusting the dosage of the phosphorus implant.

ACKNOWLEDGMENTS

The authors would like to thank S. S. Lau of the University of California (San Diego) for helpful discussions. This work was supported by a Competitive Earmarked Research Grant from the Research Grants Council of Hong Kong and the Hong Kong Industry Department.

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