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Temperature effects on the properties of Ge thin films

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The effects of substrate temperature (T_s) on the properties of vacuum evaporated p-type Ge thin films have been investigated for $25 < T_s < 400\,^\circ$C. Increase in the substrate temperature improves the crystallinity and increases the grain size resulting a gradual change from amorphous to polycrystalline structure which was attained above a substrate temperature of 225 °C. Low resistive (1×10^{-2} ohm-cm) and high mobility (280 $\text{cm}^2/\text{V} \cdot \text{s}$) films were obtained at $T_s = 400\,^\circ$C. It has been observed that the conduction mechanism in polycrystalline films was dominated successively by hopping, tunneling and thermionic emission as the sample temperature was increased from 40 to 400 K. In amorphous samples, conduction was described in terms of different hopping mechanisms.

1. Introduction

In addition to its historical importance, Ge films, including nanostructures [1, 2], grown by different techniques such as UHV-CVD [3], MBE [4], cluster-beam evaporation [1], low temperature solid phase crystallization [5], on various substrates like Si [2–4], GaAs [6] and ZnS [7] are being studied recently. Cryogenic thermometers for turbulence measurements [8], point contact warm carrier devices [7] and cryogenic resistance temperature sensors [6] are a few of the new application areas of Ge film based devices. As in most semiconducting thin films, crystallinity nature of Ge films strongly depends on the method and the conditions of growth. Polycrystalline and epitaxially grown films are highly conducting, always exhibit p-type conductivity and relatively high mobilities after the application of heat treatment at high temperatures. On the other hand, low substrate temperatures result in poorly conducting and low mobility amorphous films. Due to difficulties and uncertainties involved in the Hall measurements in amorphous materials, conflicting results on the transport properties of Ge films have been reported.

In the present work, the effects of substrate temperature on the structural and transport properties of thermally evaporated Ge thin films are reported. The results obtained from the temperature dependent Hall and conductivity measurements are used to investigate the electrical transport mechanism in a wide temperature range of 40–400 K.

2. Experimental

Thin films of Ge in Hall-bar and Van der Pauw geometries were grown by thermal evaporation of p-type bulk material from a tungsten basket at 10^{-6} torr on ultrasonically cleaned glass substrates (19 × 23 mm). Various substrate temperatures (T_s) in between 25–400 °C were applied. The average deposition rate was around 0.5 nm/s. Thickness of the films was measured by interferometric method. Structural information was obtained by TEM studies. Electrical contacts were made by evaporation of high purity aluminum on the film under vacuum and then by soldering the copper leads. The contacts were post heated, prior to soldering of the copper wires, under a nitrogen atmosphere for about 15 min at the same substrate temperature used in growth to obtain stable characteristics. The ohmic nature of the contacts was confirmed over the temperature range studied by their symmetrical and linear I-V characteristics. The dc conductivity and Hall measurements were performed using a Keithley 619 differential electrometer, a Keithley 220 constant current source and a Walker Magnion electromagnet giving up to 1 T. The temperature of the sample was controlled using a Lake Shore close cycle refrigeration system. The dc conductivity and Hall data, at room and liquid nitrogen temperatures, obtained by this system were also verified with those measured by a Bio-Rad HL5200 Hall measurement system.

3. Results and discussion

The electrical transport properties of pinhole free and well sticking Ge films were found to be independent of thickness in the range 0.3–1.0 μm. The analysis of the diffraction patterns and TEM micrographs have shown that films grown at a substrate temperature of $T_s = 25\,^\circ$C have amorphous structure and above $T_s = 100\,^\circ$C polycrystalline phase starts to form gradually yielding poly-Ge films at $T_s \geq 225\,^\circ$C . The average crystallite size increases from 50 to 350 Å as T_s increases from 100 to 400 °C.

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In general, Ge films grown at low substrate temperatures are amorphous and the increasing substrate temperature results in better crystallinity and orientation yielding a polycrystalline material. However, the substrate temperature ranges over which amorphous or polycrystalline phases dominate reported in literature vary in a remarkably wide range, since the microstructure depends strongly on the method of growth, type of the substrate and the growth conditions such as deposition rate, vacuum level, etc. For example, Ge films grown on quartz substrates at $T_s \geq 400\,^\circ\mathrm{C}$ [9], and on $\mathrm{Si_3N_4}$ coated Si substrates at $T_s \geq 290\,^\circ\mathrm{C}$ [5] were reported to have polycrystalline structure after annealing at 800 °C and 350 °C, respectively. On the other hand, poly-Ge films were obtained on ZnS substrates at $T_s \geq 400\,^\circ\mathrm{C}$ without post annealing by Uchida *et al.* [7]. In the present work, polycrystalline structure was obtained at relatively low temperatures ($T_s \geq 225\,^\circ\mathrm{C}$) with no post heat treatment (except the curing of the contacts at the same temperature as the substrate temperature applied during the growth) as compared to above mentioned records. The average grain sizes are nearly the same.

In Table I, some representative values (average of the results obtained on the samples from at least three different growth cycles with the same growth conditions) of the electrical resistivity and carrier concentration are given. These values were obtained from the room temperature dc conductivity and Hall effect measurements on films grown at different substrate temperatures. Both the thermoelectric and the Hall effect measurements have shown that all the samples exhibit p-type conduction regardless of the substrate temperature. This agrees well with earlier observations that independent of nature and conductivity type of the source material, evaporated Ge films show p-type character.

The variation of resistivity with respect to substrate temperature is given in Fig. 1. Resistivity of the amorphous films grown at $T_s = 25\,^\circ\mathrm{C}$ is around 1.2×10^3 ohm-cm. Resistivity follows a slight decrease down to 2.5×10^2 ohm-cm as T_s is increased up to 200 °C. Further increase of T_s results in a markedly decrease in resistivity and at $T_s = 400\,^\circ\mathrm{C}$ highly conducting ($\rho \approx 1 \times 10^{-2}$ ohm-cm) films were obtained.

From the Hall measurements, average free carrier concentration p at room temperature was found vary from 10^{14} to 10^{19} $\mathrm{cm^{-3}}$ for various substrate temperatures. Temperature dependent Hall data indicated that for films grown at low T_s hole concentration p increases rapidly with temperature. For example, for A type samples increase in p is more than five orders of magnitude, see Fig. 2. Temperature dependence of p becomes weaker as T_s is increased and for $T_s \geq 225\,^\circ\mathrm{C}$, p becomes almost temperature independent. For these samples both the conductivity and the effective mobility have the same activation energies.

TABLE I Some parameters of Ge thin films measured at room temperature

Sample	$T_{\mathrm{sub}}(^\circ\mathrm{C})$	$t(\mu\mathrm{m})$	$\rho(\Omega\cdot\mathrm{cm})$	$p(\mathrm{cm^{-3}})$
A	25	0.98	1.2×10^3	2.3×10^{14}
B	100	0.55	6.3×10^2	4.3×10^{14}
C	150	0.97	5.1×10^2	2.3×10^{15}
D	200	0.57	2.5×10^2	3.1×10^{17}
E	225	0.44	3.2×10^{-1}	3.0×10^{19}
F	300	0.73	6.6×10^{-2}	4.9×10^{18}
G	400	0.30	1.3×10^{-2}	1.7×10^{18}

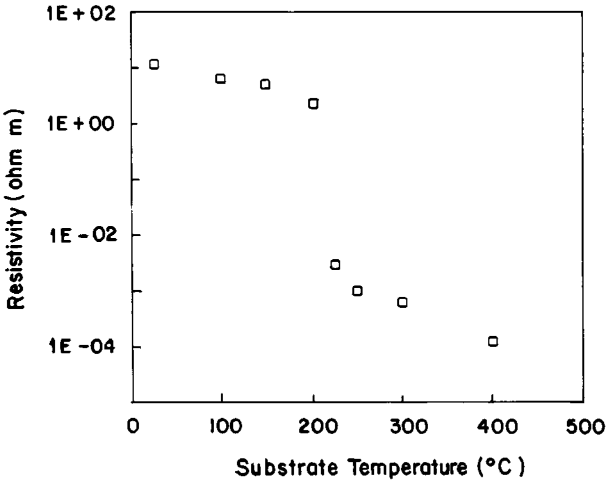

Figure 1 Substrate temperature dependence of resistivity.

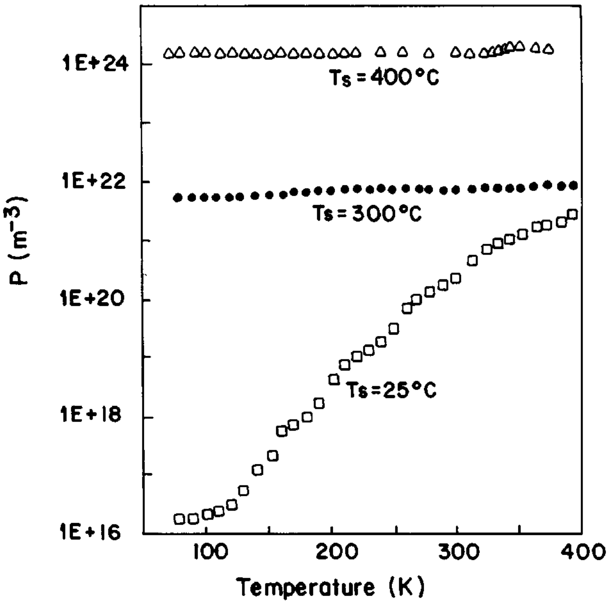

Figure 2 Temperature dependence of the carrier density.

The Hall mobility at room temperature, calculated from the simultaneous Hall and conductivity measurements, was found exhibit a minima around $p \approx 10^{17}$ $\mathrm{cm^{-3}}$. Thus the films having higher carrier densities, i.e. the films grown at $T_s \geq 225\,^\circ\mathrm{C}$ have partially depleted grains and the Hall coefficient measures the average carrier density in the grains [10].

The highest Hall mobility observed in the present work is 280 $\mathrm{cm^2/V \cdot s}$ in samples grown at $T_s = 400\,^\circ\mathrm{C}$. Some of the recently reported mobility values are; 100 $\mathrm{cm^2/V \cdot s}$ in Ge films grown at $T_s = 600\,^\circ\mathrm{C}$ (which increases to 250 $\mathrm{cm^2/V \cdot s}$ after a heat treatment at 900 °C) [9], and 360 $\mathrm{cm^2/V \cdot s}$ in films grown at $T_s = 600\,^\circ\mathrm{C}$ [5]. Comparison of these values with that obtained in the present work shows that a relatively high mobility can be obtained without annealing and at

TABLE II Mott's parameters

Sample	A	B	C	D	E	F	G
$N(E_F)$ (cm^{-3}/eV)	1.8×10^{22}	2.8×10^{19}	6.3×10^{21}	1.4×10^{23}	4.3×10^{28}	2.4×10^{27}	3.0×10^{31}
$\gamma(cm^{-1}) \times 10^9$	0.85	0.84	0.56	1.3	15.0	4.1	39
T_0(K)	7.2×10^6	4.3×10^6	5.7×10^6	3.7×10^6	1.6×10^4	5.9×10^3	4.1×10^2
R(100 K) (cm)	4.1×10^{-8}	3.6×10^{-7}	5.8×10^{-8}	2.2×10^{-8}	5.1×10^{-10}	1.4×10^{-9}	7.7×10^{-11}
γR	3.5	3.0	3.3	2.9	7.5	5.9	3.0
W(100 K) (meV)	200	170	190	170	43	34	17

relatively low substrate temperatures, which is promising for device applications.

To investigate the conductivity mechanism in our samples we have analyzed the data obtained from the temperature dependent conductivity studies in the range 40–400 K. It was observed that, in general, in all films conductivity is thermally activated. However, the temperature dependence of conductivity exhibits different characteristics below and above 125 K, approximately. In the low temperature region both amorphous and polycrystalline films behave similarly. At temperatures above 125 K, different conduction mechanisms take place in different structures. The detailed analysis of the conduction mechanism is given below.

(i) $T < 125$ K amorphous and polycrystalline films: Temperatures below 125 K, temperature dependent conductivity data were found show good fit to the Mott's expression [11]

$$\sigma\sqrt{T} = \sigma_0 \exp[-(T_0/T)^{1/4}] \qquad (1)$$

in which the pre-exponential factor is

$$\sigma_0\sqrt{A^2 N(E_F)/\gamma}, \qquad (2)$$

where $A = 3e^2\nu\sqrt{8\pi k}$, ν being the phonon frequency, and the degree of disorder,

$$T_0 = \frac{16\gamma^3}{kN(E_F)} \qquad (3)$$

are related to the density of localized states $N(E_F)$ and to the wave function decay constant γ through the Equations 2 and 3. Both σ_0 and T_0 were obtained from the temperature dependent conductivity data below 125 K by plotting $\ln\sigma\sqrt{T}$ vs. $T^{-1/4}$ (some of which are shown in Fig. 3). These values were used to evaluate Mott's parameters [11, 12] by assuming a phonon frequency of $\nu = 10^{13}$ s^{-1}, see Table II. In this table R and W represent the hopping distance and the average hopping energy, respectively. In order to conclude that the electrical conduction mechanism can be explained by the Mott's localized state model, the following criteria; $\gamma R \gg 1$, $W \gg kT$ and $T_0 > 10^3$ must be fulfilled. Examination of Table II shows that except for the samples grown at $T_s = 400\,°C$, Mott's parameters reasonably satisfy above requirements and our results are comparable to those reported earlier for a restricted temperature range for rf-sputtered Ge thin films [13]. The degree of disorder (as represented by T_0) decreases with increasing substrate temperature, supporting the idea that crystallinity and average grain size are both increasing with increasing T_s as concluded from the structure studies. One may further argue that this is also one of the reasons that lies behind the quite consistent decrease observed in W (the energy required for hopping at a given temperature) with increasing T_s.

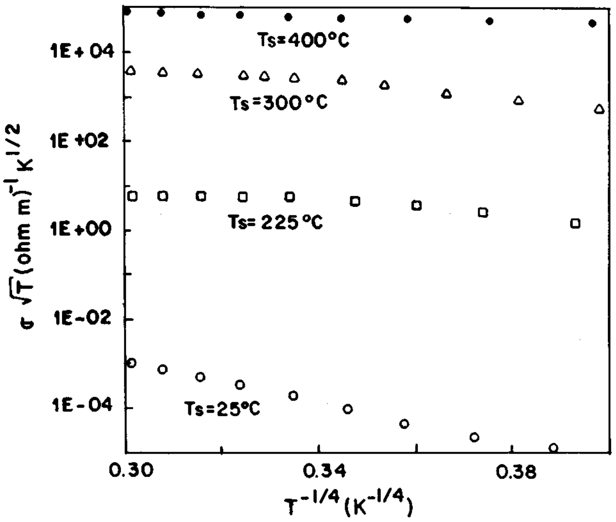

Figure 3 Temperature dependence of the conductivity below 125 K.

Based on the above analysis of the temperature dependent conductivity data, conduction mechanism both in amorphous and polycrystalline films at low temperatures can be explained as follows. The trapping states generated by the disordered atoms and dangling bonds are distributed in the band gap. The states below the pinned Fermi level are filled and therefore charged. The states above it are empty and may capture carriers only from the filled trap states, since at low temperatures there are no available carriers from the valence band. The hopping of charge carriers from occupied trap states to empty ones will then be the dominant conduction mechanism. In addition, carriers released from the filled trap states contribute to the conduction.

(ii) $T > 125$ K, polycrystalline films: In this region, conductivity of the films grown at $T_s \geq 200\,°C$ were found to be thermally activated following the rule

$$\sigma\sqrt{T} = \sigma_0 \exp(-E_\sigma/kT), \qquad (4)$$

where σ_0 is the pre exponential factor and E_σ is the activation energy of conductivity. In Fig. 4 semilogarithmic plots of $\sigma\sqrt{T}$ vs. T^{-1} for various samples grown at different substrate temperatures are given. For a sample grown at a specific substrate temperature this plot showed linear variation in three different temperature

TABLE III Activation energy of conductivity, E_σ (meV) in different temperature ranges

	Sample			
T(K)	D	E	F	G
125–200	71	37	18	9
200–300	119	61	36	14
300–400	219	89	44	20

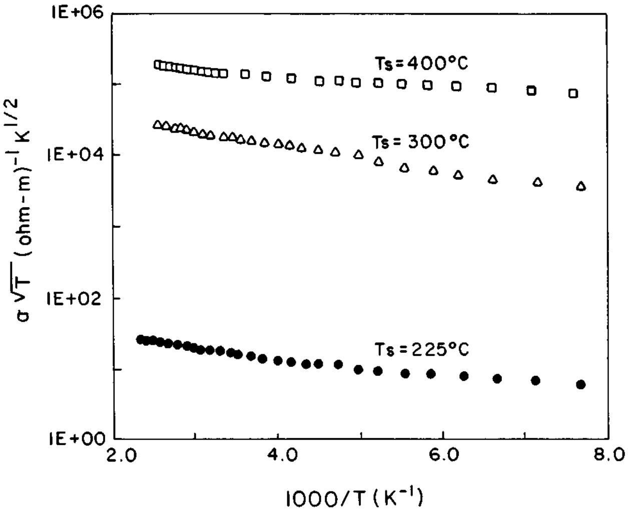

Figure 4 Temperature dependence of the conductivity above 125 K (polycrystalline samples).

regions; 125–200, 200–300 and 300–400 K, from the slopes of which E_σ values were calculated and shown in Table III. The tabulated values have standard error of at most 4 meV as calculated from the linear regression of $(\ln \sigma \sqrt{T})$ vs. T^{-1} data. The activation energy of conductivity was found to vary from 9 to 220 meV depending on the substrate temperature. The general tendency is that E_σ is comparatively higher in the higher temperature region. Furthermore, in each temperature region, E_σ decreases with increasing substrate temperature.

In polycrystalline structure at the grain boundaries, atoms are disordered and due to incomplete atomic bonding large number of defects and hence trapping states are produced. When these states trap mobile carriers they become charged and as a result potential barriers will be created at the grain boundaries. In samples for which $E_\sigma > kT$, the current transport, in the related temperature interval, is limited by the these barriers and governed by the thermionic emission of carriers over the grain boundary potentials (especially when the grains are completely depleted corresponding to low p values with high thermal activation). On the other hand, when $E_\sigma < kT$, thermionic emission theory is not applicable. In this case σ vs. T^2 plots were found to be linear up to 190, 200 and 260 K for E, F and G type samples, respectively (see Fig. 5). Thus, above 125 K, tunneling of carriers through the potential barriers [10, 14–16] is the dominating conduction mechanism up to some temperature above which the thermionic contribution becomes more important. The range over which the tunneling contribution is dominant widens with the increasing hole concentration (corresponding to partially depleted grains).

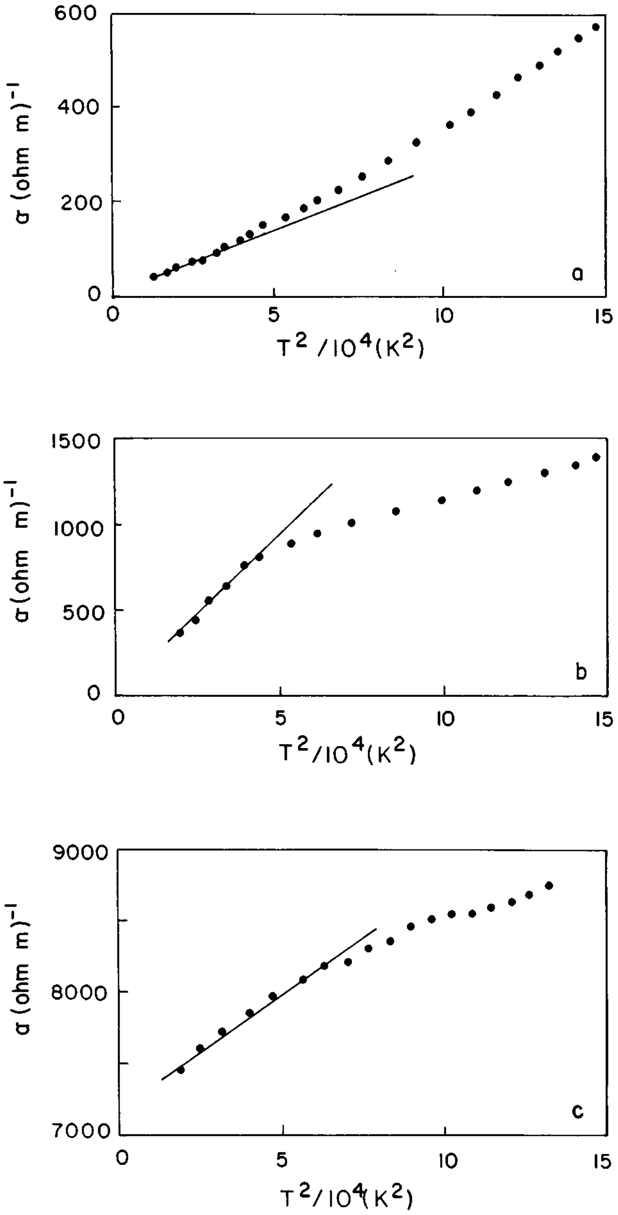

Figure 5 Conductivity data as a function of T^2 on (a) E, (b) F and (c) G type samples. Linear portions are shown by straight lines.

(iii) $T > 125$ K, amorphous films: In this region, conductivity data of amorphous films were found to obey

$$\sigma = \sigma_0 \exp(-\Delta E/kT),$$

where σ_0 is a constant and ΔE is the activation energy for carrier transfer. From $\ln \sigma$ vs. T^{-1} plots, ΔE was found to vary around 180–290 meV for samples grown at different substrate temperatures. These values, being small as compared to $\frac{1}{2}E_g$, suggest that the two possible mechanisms for the electrical conduction are tail states conductivity involving arbitrary energy levels in the tail of the valance band and hopping conductivity involving strongly localized states at the mid-gap.

4. Conclusions

It was found that Ge thin films can be grown by thermal evaporation in polycrystalline structure for substrate temperatures as low as 225 °C. Improvement in the electrical properties with the increasing substrate temperature was found to be supported with the corresponding changes in the microstructure as analyzed by TEM studies. Hall mobility of 280 $\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ obtained in films grown at $T_\mathrm{s} = 400\,^\circ\mathrm{C}$, without the need of annealing at temperatures higher than the substrate temperature, is remarkably high.

Conduction mechanism in amorphous samples was found to change gradually from variable range hopping to hopping to the nearest neighbors and then to thermal excitation to tail states, as the temperature increases from 40 to 400 K.

In polycrystalline samples, conduction was best described by the variable range hopping at low temperatures. Above 125 K, as temperature increases, tunneling followed by thermionic emission were found to be the dominant conduction mechanisms.

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