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Electrical properties of phosphorus diffused GaAs

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The electrical parameters, i.e. mobility, resistivity and ionization energy, of the dopant (Se) have been determined at different depths in phosphorus diffused GaAs. These values have been compared with those obtained for the epitaxially grown specimens.

1. Introduction

Because of its many applications in various devices, such as semiconductor laser diodes operating to the visible region, light emitting diodes, high power diodes, etc., a number of methods to produce $GaAs_{1-x}P_x$ have been investigated during the last two decades [1–5]. The characterization of $GaAs_{1-x}P_x$ produced by different methods is, therefore, essential to determine its compatibility as the base material in these devices. Its properties, i.e. electrical, optical, structural, etc., in the specimens grown by the methods given in [1–5] have already been studied extensively by earlier workers [6–8]. The same is not, however, true for $GaAs_{1-x}P_x$ prepared by phosphorus diffusion in GaAs [9–11]. The purpose of this work is to study the electrical properties of phosphorus diffused GaAs to know its comparability with the epitaxially grown $GaAs_{1-x}P_x$.

When phosphorus is diffused in GaAs at pressures $\geqslant 8$ atm, $GaAs_{1-x}P_x$ is formed [9–11] such that the phosphorus content in the diffused region changes with depth and hence the measurements at different depths are required to study the changes occurring in electrical properties at different compositions.

2. Experimental procedure

2.1. Preparation

Phosphorus was diffused in lapped and chemically polished GaAs single crystal specimens (5 mm × 5 mm) and the diffused specimens were cleaned in a manner described elsewhere [9]. The formation of $GaAs_{1-x}P_x$ after diffusion was confirmed by X-ray and reflectivity measurements taken on the diffused specimens [9]. A few microns were lapped-off from the sides of the specimens to eliminate the effect of side layers on the resistivity and Hall measurements.

2.2. C–X profiles

The composition–depth profiles of the specimens diffused at 800, 1000 and 1100° C are given in Fig. 1. These have been obtained by taking the reflectance spectrum of the surfaces of these specimens obtained after successive lapping [9].

2.3. Ohmic contacts

Cleaned n-type specimens were coated with Sn by vacuum evaporation followed by electroless Ni plating from standard solution at 90° C for 2 min. The specimens were then alloyed in H_2 at 500 to 550° C for about 5 min, which gave the minimum contact resistance value. Pre-dipping in $SnCl_2$ and $PdCl_2$, as described by Pearlstein [12], was not needed on tin coated specimens.

2.4. Resistivity measurements

The resistivity measurements were taken by four points probe method [13]. The ohmic contacts for these measurements were made in the form of four small dots of 0.5 mm diameter arranged in a straight line such that centre-to-centre inter-dot spacing was 1 mm. The potential drop (V) across the inner two dots was measured when a current (I) was flowing through the outer dot contacts.

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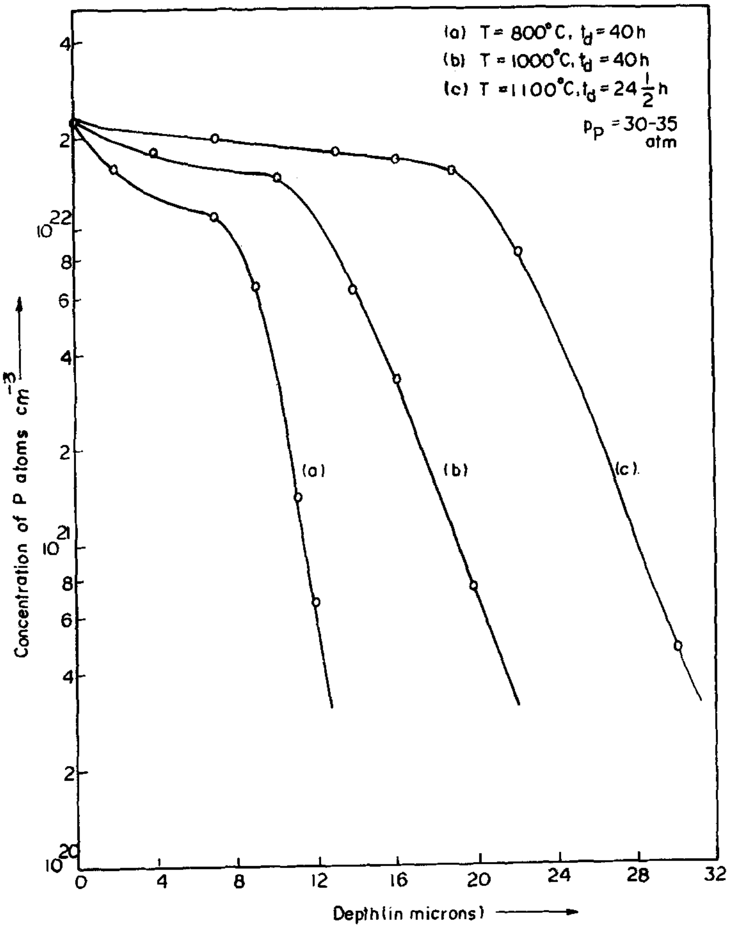

Figure 1 Phosphorus concentration – depth profiles obtained from reflectance studies.

The $V/I\rho_2$-depth profiles (ρ_2 being the resistivity of parent GaAs) were obtained for the specimens diffused at 800° C for 40 h and at 1000° C for 24 h by taking such measurements after the removal of successive layers by lapping and making alloyed contacts on the lapped surfaces in the above-mentioned manner. The layer resistivities were computed using the relation;

$$\frac{V}{I\rho_2} = \frac{\rho_1}{\rho_2} \cdot \frac{\text{C.F.}}{2\pi}$$

where C.F. is a correction factor described later in the Appendix. Further, since the alloyed dot contacts had finite geometry, another correction factor was needed to know the absolute values of resistivities. However, in the present investigation, these values have been described in terms of resistivity ratios and all the resistivity measurements were taken with identical alloyed dots which eliminates the latter correction factor. However, this assumes that this correction factor is independent of the resistivity of the layer.

2.5. Hall measurements

Hall measurements at different depths were taken on the diffused specimens by Van der Pauw's method [15]. Four small alloyed contacts were made at the corners of the specimens in the above mentioned manner and the leads were taken out from these dots by soldering four small indium balls (0.5 mm diameter) with them. The Hall measurements at each depth were taken in a magnetic field of 0.25 weber m^{-2} when a d.c. current $\leqslant 10$ mA was passing through the two contacts. The corresponding Hall voltage developed across two contacts was measured with the help of a Keithley Microvoltmeter. In order to eliminate the effects of stray electric fields, measurements were repeated with reversed magnetic field. Voltages, currents and magnetic field could be measured with an accuracy within a few percent.

3. Results

Since $GaAs_{1-x}P_x$ formed after diffusion had higher resistivity than the parent GaAs beneath it, the measured resistivity values were corrected

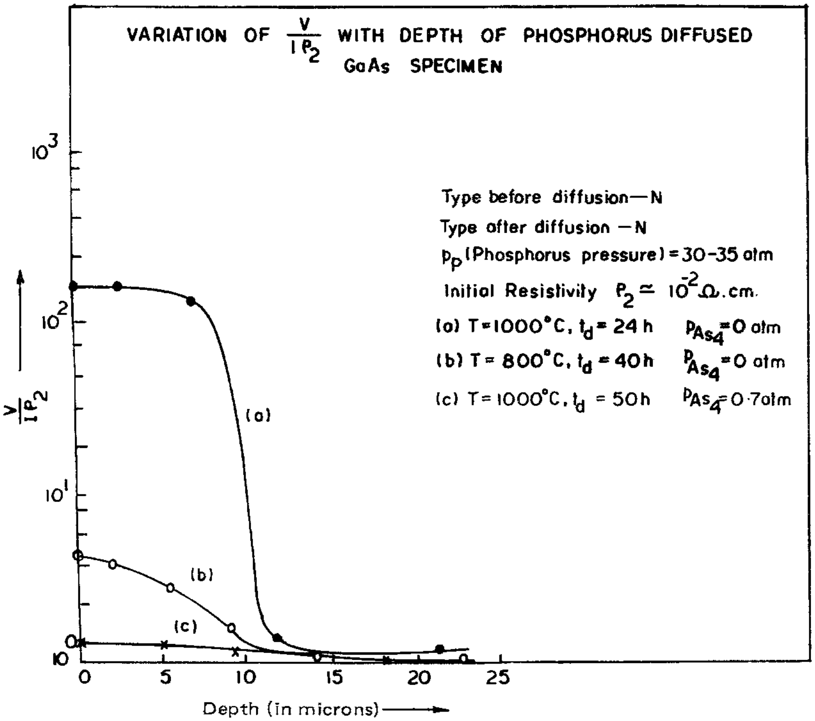

Figure 2 $V/I\rho_2$ variation as a function of depth for different phosphrous diffused specimens.

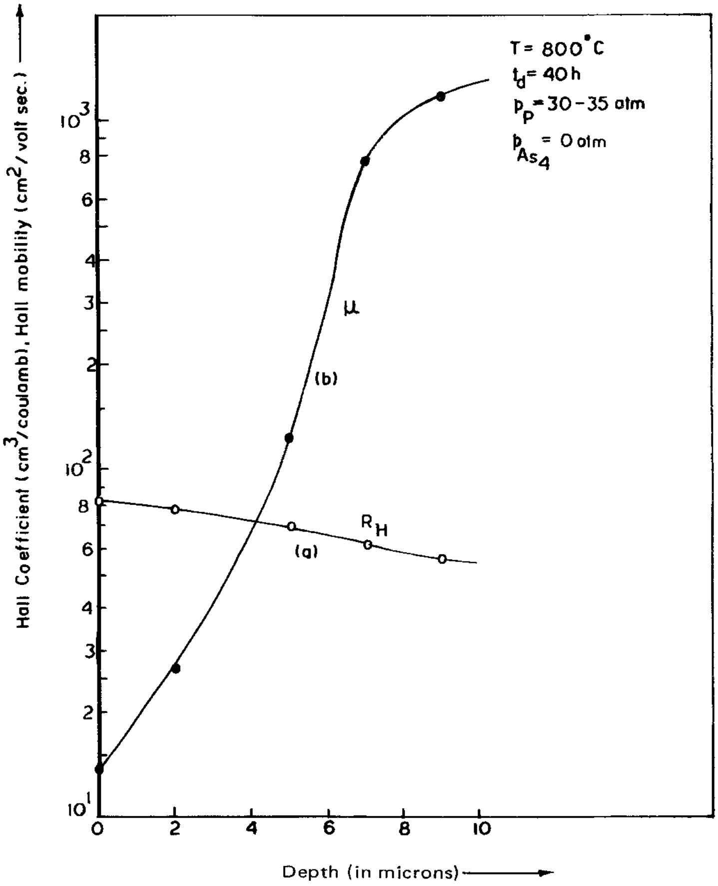

Figure 3 (a) Hall coefficient (R_H) as a function of diffusion depth. (b) Hall mobility (μ) as a function of diffusion depth.

for the large leakage current passing through the parent GaAs layer. The correction factors for the specimen having high resistivity surface layer and low resistivity bottom layer have been computed by solving Laplace's equation. The analysis as well as the correction factor graphs are given in the Appendix. The $V/I\rho_2$-depth profiles of the specimens diffused at 800 and 1000° C for time durations cited above are given in Fig. 2. As can be seen from Fig. 2a and b, $V/I\rho_2$ does not change significantly with depth in the region 0 to 10 μm for specimen (a) and 0 to 5 μm for the specimen (b) and then attains the initial value of the undiffused specimen after 12 μm. The composition–depth profiles obtained on these diffused specimens also show a similar behaviour (Fig. 1), i.e. the composition of $GaAs_{1-x}P_x$ does not change substantially in the initial region where $0.7 \leqslant x \leqslant 1.0$ and then falls off rapidly. The resistivity in this region is not expected to show a substantial change for a given carrier concentration because there is only marginal variation of mobility in the composition range $0.7 \leqslant x \leqslant 1.0$ [6, 7] and as will be shown later, it is the mobility which mostly determine the resistivity. Therefore, a two layer resistivity structure with the diffused layer forming a higher resistivity surface layer and the undiffused bottom as the lower layer is the result of the phosphorus diffusion. The $V/I\rho_2$ of the specimens diffused at 1000° C in the presence of excess As remained unchanged and was nearly unity.

The variation of the Hall coefficient and mobility with depth in the diffused region of the specimens diffused at 800° C for 40 h is shown in Fig. 3. The mobility values obtained this way are comparable in order of magnitude with that of epitaxially grown specimens at various compositions corresponding to various depths of diffusion. However, in case of Hall measurements taken on a resistivity structure of the type formed here, no correction factor for the leakage current is needed, because it has already been shown by Patrick [16] that this correction factor is not very significant. Whatsoever significance it might have, is lost in the present complex system where only average values are obtained during the measurements.

The Hall measurements taken on the specimen diffused at 1000° C gave ambiguous results probably because of the reasons given below and, therefore, are not included in the graphs.

4. Determination of ionization energy

From the known values of the carrier concentration (determined by Hall measurements) before and after diffusion, the ionization energy of the dopant (Se) already present in parent GaAs could be determined at different compositions of the diffused $GaAs_{1-x}P_x$ as follows. The carrier concentration, when N_d donors and N_A ionized acceptors are present, is given by [17];

$$n = \frac{N_d}{1 + 2\exp(E_f - E_d)/kT} \tag{1}$$

which gives

$$E_d = E_f + 2.303\,kT\log\left[\frac{2(n+N_a)}{N_d - n - N_A}\right] \tag{2}$$

In these equations, E_f is the Fermi energy, k is the Boltzmann's constant, T is the temperature in K and N_a is the number of unionized acceptors. Substituting $n = 1.2 \times 10^{17}\ \text{cm}^{-3}$, $N_A = 0.7 \times N_d$ (given) and E_d(ionization energy of Se in GaAs) = 0.005 eV, we get, $N_d = 4.0 \times 10^{17}$ cm^{-3} in the undiffused specimen. The values of E_f was derived using the relation;

$$n = \frac{4}{\sqrt{\pi}}\left[\frac{2\pi m^* kT}{h^2}\right]^{3/2} \cdot f_{1/2}(E_f/kT) \tag{3}$$

where m^* is the effective mass of the electron in the conduction band ($m^* = 0.072\,m_0$ in GaAs).

The donor concentration cannot change during diffusion of phosphorus in GaAs, although the carrier concentration may be affected because of different ionization energies of the carriers in the diffused phosphorus-rich regions. The carrier concentration for different compositions of $GaAs_{1-x}P_x$ in the diffused region are known from the Hall measurements. Therefore, E_d can be computed from Equation 2 by substituting the respective values of n, N_A and N_d. In the composition range of $x \geqslant 0.7$, m^* was taken as $1.4\,m$ [18] corresponding to the assumption that the number of (1 0 0) minima in the conduction band was $z = 6$. With decreasing phosphorus content in $GaAs_{1-x}P_x$ i.e. $x \leqslant 0.7$, the energy separation between (0 0 0) and (1 0 0) minima decreases. Therefore, the distribution of electrons in two sub-bands has to be reconsidered. In this case, the experimental values of the Hall coefficient R and the carrier mobility are given by the following expressions [18];

$$R = \frac{R_0(1+b^2c)\cdot(1+c)}{(1+bc)}$$

and

$$\mu = \frac{(1+b^2c)}{b(1+bc)}$$

and Equation 1 is then modified to

$$n_1 + n_2 = \frac{N_\mathrm{d}}{1 + 2\exp\left[\dfrac{E_\mathrm{f} - (\Delta E_{12} - E_\mathrm{d})}{kT}\right]}$$

The calculations were performed using the values of m_1 and m_2 and ΔE_{12} given by the relations, $\Delta E_{12} = 036 - 0.80x + (6 \pm 2).\ 10^{-5}\,\mathrm{eV}$ (at $T = 300\,\mathrm{K}$); $m_2 = 1.4m$, $m_1 = 0.072\ (1+x)m_0$.

TABLE I

Depth (μm)	Diffused layer	Epitaxial compositions	Ionization energy (eV)
0	600.0	100.0	0.093
2	300.0	100.0	0.087
5	56.0	25.0	0.07
7	8.0	2.1	–
9	5.0	1.0	–

The ionization energies of Se at different depths of $GaAs_{1-x}P_x$ prepared by diffusion are listed in Table I. The values obtained this way, if compared with that of epitaxially grown compositions corresponding to these depths [18], differ slightly for $1.0 \geqslant x \geqslant 0.5$. However, the agreement is rather surprisingly good in view of the limitations of the Hall measurements in a sample of varying phosphorus content.

5. Discussion

Ku [6] and others [7] have shown that the electron mobility in $GaAs_{1-x}P_x$ is a function of its composition. The dopant Se, which is present in the parent GaAs, remains n-type in $GaAs_{1-x}P_x$ and the carrier concentration does not change substantially as a result of P diffusion (Fig. 3). Therefore, the resistivity value in the diffused specimen will mainly depend on the mobility of the carriers and hence the composition dependence of the mobility will mainly determine the resistivity. The results of the epitaxial compositions have been compared with the corrected average resistivity values obtained with the decreasing thickness of the diffused layer (Table I).

Since at the surface, there is almost 100% phosphorus, i.e. the top-most layer is GaP (Fig. 1);

$$\rho_\mathrm{diff} = \frac{1}{ne\mu_\mathrm{GaP}}$$

and

$$\mu_\mathrm{GaP} \simeq 50 - 100\ \mathrm{cm^2\,V^{-1}\,sec^{-1}}.$$

$$\mu_\mathrm{GaAs} \simeq 5000 - 8000\ \mathrm{cm^2\,V^{-1}\,sec^{-1}}$$

hence,

$$\frac{\rho_\mathrm{diff}}{\rho_\mathrm{GaAs}} \simeq \frac{\rho_\mathrm{GaP}}{\rho_\mathrm{GaAs}} \simeq \frac{5000}{50} = 100.$$

The corrected value obtained for the specimen diffused at 800° C is ~ 600. The abnormally high corrected values of the resistivity in the diffused region of the specimen diffused at 1000° C may arise due to quenched-in vacancies at As or P sites which act as p-type dopant $GaAs_{1-x}P_x$ [19, 20] resulting in compensation. The ambiguous results of the Hall measurements in the same specimen can also be due to the above-mentioned reason.

The resistivity results of the specimen diffused in the presence of excess As at 1000° C for 50 h can also be explained on the basis of mobility-composition profiles of epitaxially grown $GaAs_{1-x}P_x$. The surface composition of the specimen, as can be seen from the reflectivity spectrum, is $GaAs_{0.90}P_{0.10}$ [9]. According to Ku's profile [7];

$$\mu_{\mathrm{GaAs}_{0.90}\mathrm{P}_{0.10}} \simeq \mu_\mathrm{GaAs}$$

The carrier concentration, as obtained from the Hall measurements on the specimen, is $\sim 10^{17}\,\mathrm{cm^{-3}}$ which is close to the carrier concentration of the parent GaAs ($1.2 \times 10^{17}\,\mathrm{cm^{-3}}$) i.e. $n_\mathrm{undiffused} \simeq n_\mathrm{diffused}$, and therefore;

$$\frac{\rho_{\mathrm{GaAs}_{0.90}\mathrm{P}_{0.10}}}{\rho_\mathrm{GaAs}} \simeq 1.$$

It can be inferred from the carrier concentration values of the specimens diffused either in the presence or absence of excess As that it is rather unlikely for the As atoms (replaced by diffusing P atoms) to occupy the interstial sites, because if this is true, each As atom can donate five electrons, resulting in an abnormal increase in the carrier concentration value after the diffusion, which is not observed. However, the formation of neutral As vacancy–As atom pair cannot be altogether ruled out.

6. Conclusions

(1) The resistivity results can be explained by considering the mobility variation with the composition.

(2) The diffused layer formed at $T \geqslant 1000°$ C is highly compensated.

(3) The ionization energy values of Se determined at different depths of the diffused region are more or less comparable to the reported values.

Appendix

It has been assumed in the analysis that four probes placed on the specimen were equally spaced and arranged in a straight line and each current probe behaved as a point source for the potential distribution. The potential distribution at $z = 0$ when the point source is located at the surface of a medium with different layer resistivities $(\rho_1 > \rho_2 > \rho_3)$ is given by [21];

$$V_s = \frac{I\rho_1}{2\pi}\left[\frac{1}{r} + 2\int^{\infty}\frac{(k_1 e^{-2\lambda h} + k_2 e^{-2\lambda h_1}) J_0(\lambda r)\, d\lambda}{1 - k_1 e^{-2\lambda h} - k_2 e^{-2\lambda h_1} + k_1 k_2 e^{-2\lambda t}}\right].$$

When both the current sources are present on the surface, the resultant potential at probe 2 of a four point probe assembly with probe spacing r_1, r_2 and r_3 between consecutive probes can be given by;

$$V_{p_2} = \frac{I\rho_1}{2\pi}\left[\frac{1}{r_1} - \frac{1}{(r_2 + r_3)} + 2\int_0^{\infty}\frac{(k_1 e^{-2\lambda h} + k_2 e^{-2\lambda h_1})\{J_0(\lambda r_1) - J_0[\lambda(r_2 + r_3)]\}d\lambda}{1 - k_1 e^{-2\lambda h} - k_2 e^{-2\lambda h_1} + k_1 k_2 e^{-2\lambda t}}\right].$$

Similarly, the resultant potential at probes 3 is;

$$V_{p_3} = \frac{I\rho_1}{2\pi}\left[\frac{1}{(r_1 + r_2)} - \frac{1}{r_3} + 2\int_0^{\infty}\frac{(k_1 e^{-2\lambda h} + k_2 e^{-2\lambda h_1})\{J_0[\lambda(r_1 + r_2)] - J_0(\lambda r_3)\}d\lambda}{1 - k_1 e^{-2\lambda h} - k_2 e^{-2\lambda h_1} + k_1 k_2 e^{-2\lambda t}}\right].$$

Hence, the floating potential V_f between these two probes is

$$V_f = V_{p_2} - V_{p_3} = \frac{I\rho_1}{2\pi}\left[\frac{1}{r_1} + \frac{1}{r_3} - \frac{1}{(r_1 + r_2)} - \frac{1}{(r_2 + r_3)} + 2\int_0^{\infty}\frac{(k_1 e^{-2\lambda h} + k_2 e^{-2\lambda h_1})\{J_0(\lambda r_1) + J_0(\lambda r_3) - J_0[\lambda(r_1 + r_2)] - J_0[\lambda(r_2 + r_3)]\}d\lambda.}{1 - k_1 e^{-2\lambda h} - k_2 e^{-2\lambda h_1} + k_1 k_2 e^{-2\lambda t}}\right]$$

When probe spacing is equal, i.e. $r_1 = r_2 = r_3 = r$;

$$V_f = \frac{I\rho_1}{2\pi}\left[\frac{1}{r} + 4\int_0^{\infty}\frac{(k_1 e^{-2\lambda h} + k_2 e^{-2\lambda h_1})\{J_0(\lambda r) - J_0(2\lambda r)\}\, d\lambda}{1 - k_1 e^{-2\lambda h} - k_2 e^{-2\lambda h_1} + k_1 k_2 e^{-2\lambda t}}\right].$$

When correction factor (C.F.) is a function of ρ_1 and ρ_2 only, Equation 4 can be rewritten after dividing both sides by ρ_2 as;

$$\frac{V}{I\rho_2} = \frac{\rho_1}{\rho_2} \cdot \text{C.F.}$$

The correction factor was programmed for the IBM 360 computer with the following range of variables; $r = 0.1$ cm, with $0 \leqslant h \leqslant 500\,\mu$m; $t = 0.1$ cm; and $1 \leqslant (\rho_1/\rho_2) \leqslant 10^6$, and $\rho_3 = \infty$. The correction factor graphs plotted between ρ_1/ρ_2 and $V/I\rho_2$ are shown in Figs. 4 and 5. From the graphs of $V/I\rho_2$ versus h for $t = 500\,\mu$m, it is found that for $h \leqslant 100\,\mu$m, $V/I\rho_2$ does not change significantly. It is to be further noted that when $\rho_1 = \rho_2$, $V/I\rho_2$ should be ~ 1.6. However, in the present graphs, the C.F. for $(\rho_1/\rho_2) = 1$, $V/I\rho_2 \simeq 4$. This is because of the finite geometry of the specimen.

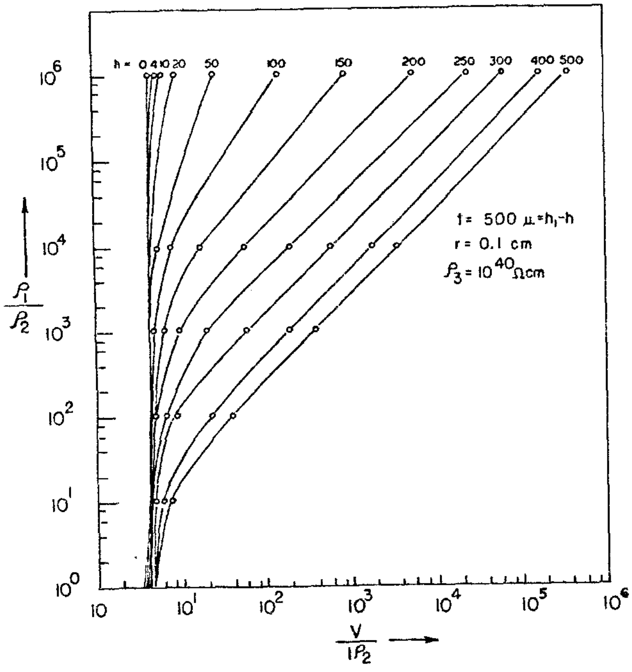

Figure 4 Correction factor graph for four-point probe resistivity measurements.

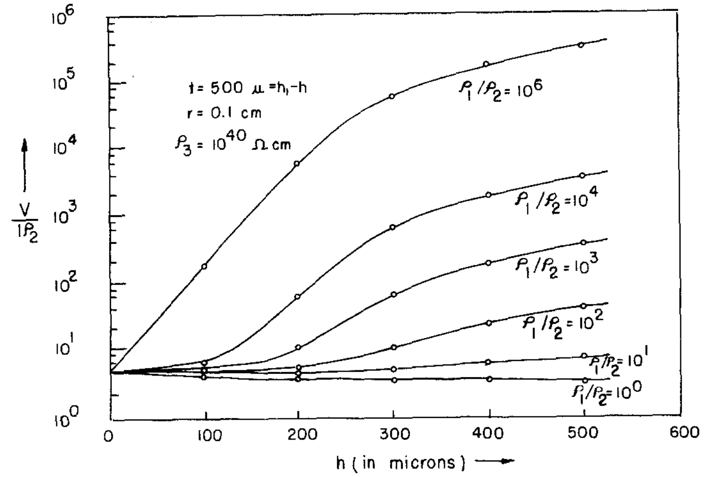

Figure 5 Correction factor graph for four-point probe resistivity measurement.

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