Selective Wet Etching of GaInP, GaAs, and InP in Solutions of HCl, CH_3COOH, and H_2O_2

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ABSTRACT

The wet chemical etching of GaInP, GaAs, and InP in solutions of $HCl:CH_3COOH:H_2O_2$ has been evaluated. In the absence of the oxidant, H_2O_2, the solutions etch InP and GaInP with high selectively over GaAs but rough surfaces are formed. When H_2O_2 is added, smoother surfaces are obtained and depending on the H_2O_2 concentration, the etchant can be made highly selective for GaAs. The etch rate of these mixtures varies strongly with the age of the solution, initially increasing and then gradually declining. The increase in etch rate is attributed to the formation of Cl_2 in solution from the reaction of HCl with H_2O_2, and the eventual decrease in etch rate to the gradual evaporation of Cl_2 from solution. The CH_3COOH in these mixtures functions as a nonaqueous solvent. In dilute solutions (1 HCl: y CH_3COOH: 1 H_2O_2, with $y \geq 20$) slow etch rates and smooth surfaces can be obtained for all three materials, suggesting that this etchant may be useful for recessing layers for heterostructure electronic and optoelectronic device applications.

Recently, GaInP has attracted attention as a wide bandgap semiconductor for electronic and optoelectronic heterostructure devices. $Ga_{0.52}In_{0.48}P$ can be grown lattice-matched to GaAs, and with a bandgap of 1.9 eV, it can potentially replace AlGaAs in devices which have been previously developed using AlGaAs/GaAs heterostructures. These devices include, for example, high electron mobility transistors (HEMTs),[1] heterojunction bipolar transistors (HBTs),[2] and various quantum well lasers.[3] A potential advantages in replacing AlGaAs with GaInP is that GaInP does not appear to exhibit problems with donor-related deep traps or DX centers which can cause instabilities in threshold voltages and transconductances of transistors.[4,5] In addition, the GaInP/GaAs heterointerface has been shown to have a dramatically lower carrier recombination velocity than that of AlGaAs/GaAs.[6]

Devices which have been fabricated from GaInP/GaAs include HBTs,[7] HEMTs,[8] and visible diode lasers.[9] In the fabrication of HEMTs or other field effect transistors a gate recess step is often required for adjusting the threshold voltage and increasing the transconductance. The requirements of a gate recess etch are that it must be slow and controllable, and result in a smooth, clean surface on which a suitable Schottky contact can be fabricated. To realize competitive devices based on GaInP/GaAs heterostructures, smooth, controllable, and material-selective etching techniques must be developed.

A solution of $HCl:CH_3COOH:H_2O_2$ in the ratio 1:2:1 has been used by Kambayashi *et al.* for rapid, smooth etching of InP.[10] In this etchant, the role of CH_3COOH is primarily that of a nonaqueous solvent for the other reactive species. In the absence of CH_3COOH rough InP surfaces result. One can substitute concentrated H_3PO_4 for CH_3COOH with somewhat similar results. Notten[1] has shown that the etch rate of InP in HCl solutions is dependent on the amount of undissociated HCl, and that aqueous solutions of HCl will not etch InP, if the concentration is less than about $6M$. He concluded that undissociated HCl molecules play a direct role in the etching mechanism, and that other etchants such as HBr and Br_2 are based on similar mechanisms.

It is well known that dilute or concentrated HCl does not appreciably etch GaAs or GaInAs but does etch native oxides on these materials.[12] However, when an oxidizing agent such as H_2O_2 or K_2CrO_4 is added to an acidic solution, GaAs will be etched, presumably by a mechanism involving continuous oxidation and oxide removal. Therefore, the selectivity of the etchant for GaAs or InP can obviously be adjusted by controlling the concentration of the oxidizing agent and undissociated HCl. The role of these reactive species on the etch rates of ternary materials like GaInP is less obvious.

We present results of wet chemical etching of GaInP, GaAs, and InP using solutions of $HCl:CH_3COOH:H_2O_2$ with varying compositions. We show that at high concentrations of CH_3COOH, these solutions etch the III-V materials slowly and smoothly. Moreover, this etchant can be made selective for either the phosphide compounds or GaAs by varying the ratio of HCl to H_2O_2.

Experimental

Materials used for the etching studies were Fe-doped InP and Cr-doped GaAs substrates, and GaInP grown on GaAs substrates by organometallic vapor phase epitaxy (OMVPE). The GaInP layers were 500 nm thick, silicon doped ($n = 1 \times 10^{17}$ cm^{-3}), and nearly lattice-matched to GaAs (nominal composition of $Ga_{0.52}In_{0.48}P$. The samples were patterned photolithographically with 100 μm squares using AZ5214 photoresist in image-reversal mode. When adequately hard-baked, the resist served as an etch mask and resisted attack well in most etchants. Etchant solutions were prepared by mixing standard solutions of HCl [36 weight percent (w/o)], H_2O_2 (30 w/o), and glacial acetic acid (CH_3COOH 99.9%) in various proportions. Typically, the HCl and CH_3COOH were premixed, and the H_2O_2 was added seconds before emersing the samples in the solution. The samples were typically etched at 20°C for 1 min without stirring or agitation, and were subsequently quenched in running deionized water and blown dry with nitrogen. The etch depth was measured using a Sloan Dektak profilometer, and the smoothness of the etched surface was evaluated by optical and scanning electron microscopy.

Results and Discussion

The effect of an oxidizing agent on the etching characteristics was examined by varying the amount of H_2O_2 in a

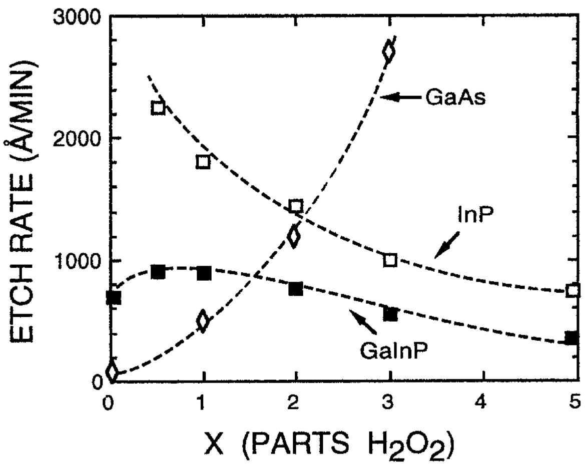

Fig. 1. Variation in etch rate of GaAs, InP, and GaInP with H_2O_2 content in mixtures of 1 HCl:20 CH_3COOH:x H_2O_2.

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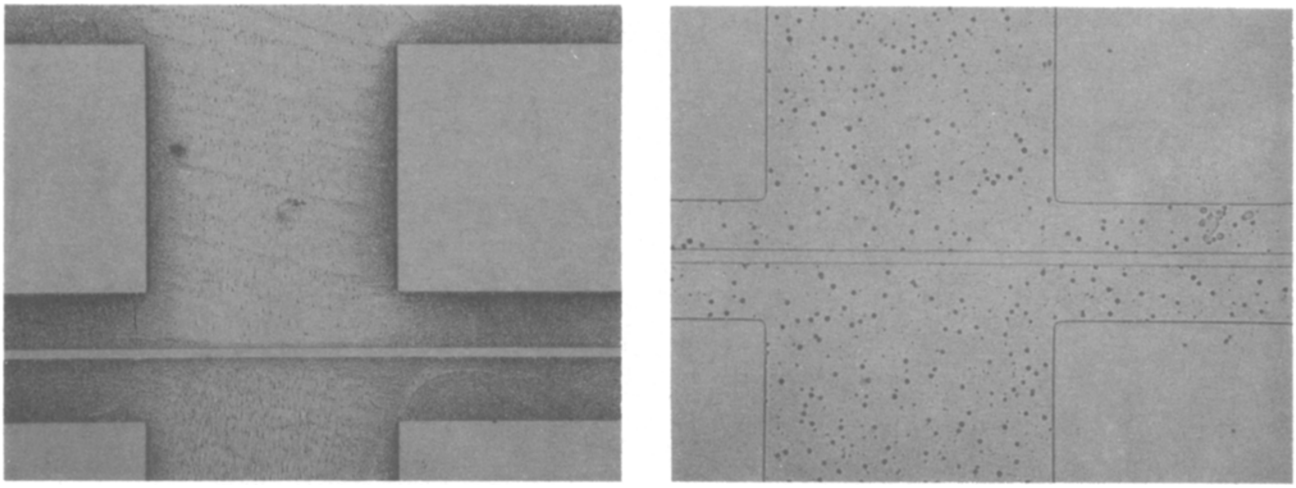

Fig. 2. Optical photograph of (a, left) InP and (b, right) GaInP rough surfaces resulting from a 2 min etch in 1 HCl:20 CH_3COOH without H_2O_2. Masked areas are 100 μm squares

mixture of 1 HCl:20 CH_3COOH:xH_2O_2, with $0 \le x \le 5$. The etch rates in Fig. 1 represent the first minute after H_2O_2 is added to the mixture. When no oxidizing agent is present, both GaInP and InP are etched selectively with respect to GaAs. The etch rates are approximately 4000, 700, and less than 50 Å/min for InP, GaInP, and GaAs, respectively.

Although highly selective, mixtures which lack an oxidizing agent leave the InP and GaInP surfaces relatively rough. Figure 2 shows Normarski micrographs of InP and GaInP etched for 2 min with $x = 0$. The surface of InP is roughest near the mask edges, and regions farther away from the mask edges show faceted hillocks indicative of anisotropic etching. In contrast to InP, surfaces of GaInP etched in this solution show convex defects which appear as small mounds on the surface. The roughness and visual haziness of these surfaces increase strongly with etch depth. The addition of a small amount of H_2O_2 ($x = 0.5$) increases the etch rate of GaAs and decreases the etch rate of InP dramatically. The decrease in the InP etch rate is consistent with the increased aqueous nature of the solution and a correspondingly greater degree of dissociation of the HCl molecules. While subsequent addition of H_2O_2 up to $x = 5$ leads to a continuous increase in the GaAs etch rate and decrease in the InP etch rate, a maximum etch rate of GaInP occurs somewhere between $x = 0.5$ and 1. Interestingly, this maximum occurs at approximately equal molar concentrations of HCl and H_2O_2 and indicates that the cations in this alloy react differently. The addition of H_2O_2 also results in a tremendous improvement in the etched surface morphology for InP and GaInP. Figures 3a and b show the surfaces of InP and GaInP, respectively, after etching for 2 min in a mixture with $x = 1$. The presence of H_2O_2 results in oxidation of the semiconductor surface. This oxidation may promote smoother surfaces by reducing crystal anisotropy near the liquid-semiconductor interface.

In solutions with equal volumes of HCl and H_2O_2 the etch rates for all three materials decrease with dilution by CH_3COOH. Figure 4 shows the etch rates in the first minute after mixing for solutions of 1 HCl: $y$$CH_3COOH$: 1 H_2O_2. With no dilution the etch depths could not be measured accurately by profilometry, because the etched surfaces were extremely rough and the masking photoresist layers were not durable in solutions this concentrated. When the solution is diluted with $y = 2$, the etched surfaces become mirror-smooth in agreement with results reported for InP etching by Kambayashi *et al.*[10]; However, the etch rate we observe for InP is approximately three times slower than they report, possibly due to differences in the age of the solution, as will be discussed in the following paragraph. In the mixture with $y = 2$, GaAs etches somewhat faster than InP and GaInP, which is characteristic of the largely aqueous nature of the etchant, *i.e.*, a greater degree of HCl dissociation. As y is increased, the etch rates for all materials decrease and the selectivity shifts from GaAs to InP. When $y = 5$, the etch rates of GaAs and InP are approximately equal, but at $y = 40$ the etch rate of InP is almost an order of magnitude greater than that of GaAs, and about twice that of GaInP. The etched surfaces of all three materials remain mirror-smooth with increased dilution by

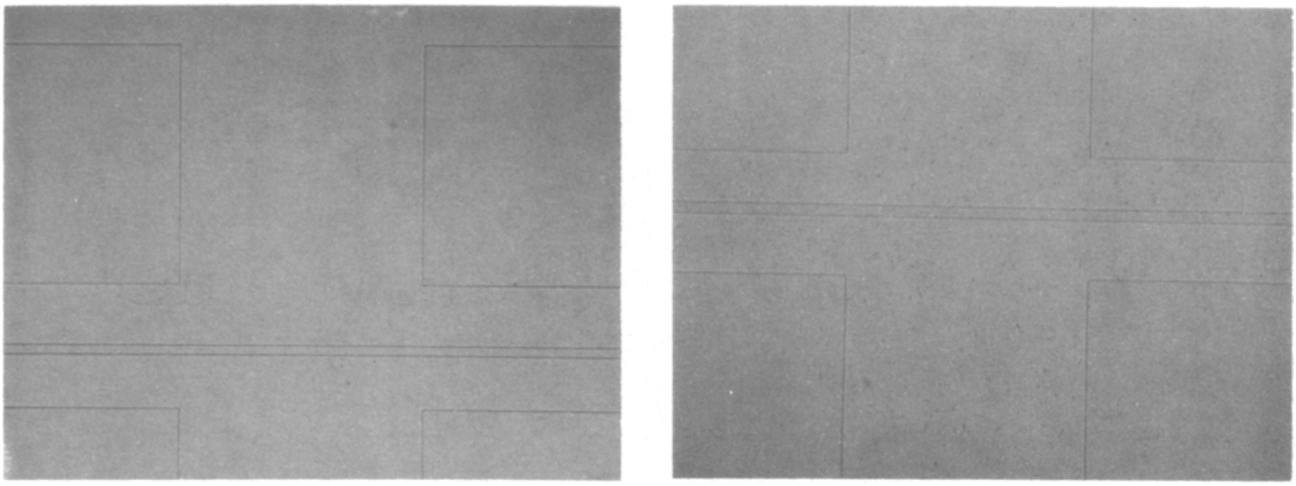

Fig. 3. Optical photograph of (a, left) InP and (b, right) GaInP smooth surfaces resulting from a 2 min etch in 1 HCl:20 CH_3COOH:1 H_2O_2. Masked areas are 100 μm squares.

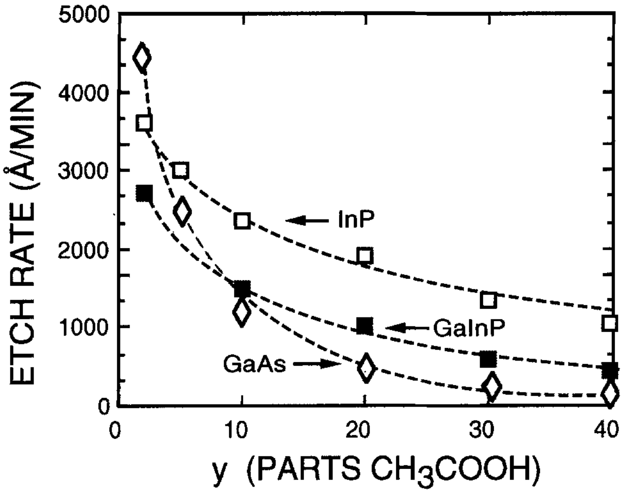

Fig. 4. Variation in etch rate of GaAs, InP, and GaInP with CH_3COOH content in mixtures of 1 HCl:*y* CH_3COOH:1 H_2O_2.

CH_3COOH, and therefore, these dilute solutions could conceivably be used for recessing GaInP donor layers in GaInP/GaAs HEMT or other field effect device structures.

To evaluate further the usefulness of these etchants for a gate recess process, the stability of a mixture of 1 HCl:40 CH_3COOH:1 H_2O_2 was evaluated by measuring the change in etch rate with the age of the solution. Fig. 5 shows that the etch rate for all materials increases strongly over the first 40 min after mixing, levels out, and then slowly decays. Initially, the relative etch rates vary as InP > GaInP > GaAs. However, within 20 min all materials etch at comparable rates showing only slight selectivity with relative etch rates GaAs > InP > GaInP. The surface morphology remained relatively smooth with increasing age of solution for all three materials.

The change in the relative etch rates suggests that a change in the dominant reaction mechanism occurs over time. One can gain insight into the changing chemical mechanisms of this system by considering the thermodynamics of chloride oxidation by H_2O_2. In aqueous solutions Cl^- is oxidized by H_2O_2, and the reactions listed in Table I can occur. The standard Gibb's free energy change, $\Delta G°$, for each reaction has been calculated from standard electrochemical potentials.[13] When considering the value of $\Delta G°$per mole of H_2O_2 consumed, the reaction producing $Cl_2(g)$ is the most favorable. Other reactions which result in chemical species containing chlorine in higher oxidation states are also highly exothermic.

However, the kinetics of all these reactions appear to be relatively slow, because it takes approximately 10 min from the time of mixing for the solution to develop a yellow tint which is indicative of Cl_2 dissolved in solution. The increase in the etch rate can be attributed to an additional reaction mechanism where molecular Cl_2 reacts directly with the III-V compounds to form soluble chlorides or oxychlorides. Additionally, the very large increase in the etch rate indicates that Cl_2 is a considerably more reactive species than HCl. The subsequent decrease in the etch rate with time is due largely to the evaporation of Cl_2 from the solution, and to a lesser extent the consumption of Cl_2 in reactions with H_2O_2 to form species such as HClO, $HClO_2$, etc. This hypothesis is supported by our observation that the mixed solution can be stored for several days in a sealed container and still retain much of its etching ability and yellow color.

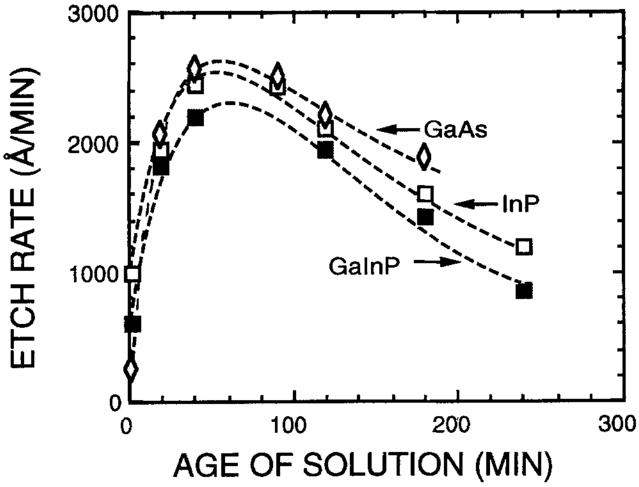

Fig. 5. Variation in etch rate of GaAs, InP, and GaInP with age of solution in mixtures of 1 HCl:40 CH_3COOH:1 H_2O_2.

Table I. Standard Gibb's free energy of reactions between H_2O_2 and Cl^-.

Reaction	$\Delta G°$ (KJ/mol H_2O_2)
$H_2O_{2\,(l)} + 2HCl_{(aq)} = Cl_{2\,(g)} + 2H_2O_{(l)}$	−80.4
$H_2O_{2\,(l)} + HCl_{(aq)} = HClO_{(aq)} + 2H_2O_{(l)}$	−56.7
$H_2O_{2\,(l)} + HCl_{(aq)} = \frac{1}{2}HClO_{2\,(aq)} + H_2O_{(l)}$	−39.8
$H_2O_{2\,(l)} + \frac{1}{3}Cl^-_{(aq)} = \frac{1}{3}ClO^-_{3\,(aq)} + H_2O_{(l)}$	−62.7
$H_2O_{2\,(l)} + \frac{1}{4}Cl^-_{(aq)} = \frac{1}{4}ClO^-_{4\,(aq)} + H_2O_{(l)}$	−74.7

The profiles of features etched in solutions of 1 HCl:*y* CH_3COOH:1 H_2O_2 show that etching is relatively isotropic when $y \geq 2$. Trenching, defined as enhanced etching near mask edges, can occur when the etch rate is limited, in part, by diffusion of reactants or products to or from the liquid-solid interface. Under these conditions regions near the mask edges etch faster due to a higher local concentration of reactants and/or a lower local concentration of products in the vicinity of the interface. As the rate of etching becomes limited, more by diffusion and less by chemical reactions at the interface, the severity of trenching increases. Trench profiles which result when etching is limited solely by diffusion have been modeled mathematically by Kuiken *et al.*[14] From their model one can infer that the severity of trenching is also highly dependent on the geometry of the sample, particularly the exposed area of the material relative to the area of the adjacent masked region.

In our experiments, the degree of trenching is affected by both the relative volume of HCl and H_2O_2 in the solution and the age of the solution. With a geometry of 100 μm masking squares separated by 100 μm spaces, trenching is virtually nonexistent when $y \leq 10$, or when the etching occurs within the first several minutes after mixing the solution. Trenching becomes somewhat more severe with higher dilution by CH_3COOH. When $y = 40$, the trenches near the mask edges can be approximately 10 to 20% deeper than the center between two masked areas. Furthermore, trenching becomes particularly acute with the increased age of the solution because of the increased contribution of Cl_2 to the dissolution process. The Cl_2 which is generated in solution is highly reactive, but present in lower concentration than the other reactants. For dilute solutions, such as $y = 40$, which are used more than 20 min after mixing, the trench depths can be more than 50% deeper near the mask edges. If using these etchant solutions for a gate recess step, trenching is of some concern. However, in devices with channel lengths of several microns or less, it is likely that trenching would be insignificant, and therefore these etchant solutions may be useful in these applications.

Summary

The chemical etching characteristics of GaInP, GaAs, and InP in solutions of HCl:CH_3COOH:H_2O_2 have been investigated. These characteristics include the variation in selectivity and etch rate with composition and age of the solution. When no H_2O_2 is present, the solution etches InP and GaInP selectively over GaAs but rough surfaces are formed. When H_2O_2 is added, smoother surfaces are obtained due to the increased role of surface oxidation, and the etchant becomes selective for GaAs due, in part, to the larger degree of HCl dissociation. The etch rate of these mixtures varies strongly with time after mixing. Etch rates increase with time initially, reach a maximum, and then gradually decline. We attribute this increase in etch rate to the formation of Cl_2 in solution via oxidation of Cl^- by H_2O_2, and the eventual decrease in etch rate to the gradual evaporation of Cl_2 from solution. Under proper conditions slow etch rates and smooth surfaces can be obtained. The results suggests that these mixtures may be useful for recessing heterostructures for electronic and optoelectronic device applications.

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Extremely Low Contact Resistivity of Ti/Pt/Au Contacts on p^+-InGaAs as Determined by a New Evaluation Method

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ABSTRACT

A convenient method for determining a low contact resistivity ρ_c is described and experimental results are presented. Small dots of p^+-InGaAs on a thick and highly conductive substrate are metallized. The corresponding boundary problem of the current distribution is solved by using an integral equation which can be evaluated numerically. This method can be used to obtain ρ_c from experimental data. The procedure overcomes the difficulties usually encountered with the transmission line method since the inhomogeneity of the current density under the contact dots is fully taken into account. The exact knowledge of the diameter of the dots is imperative and must be examined using a scanning electron microscope. The p-$In_{0.53}Ga_{0.47}As$ contact layer which is placed on a p-InP substrate ($p = 6 \cdot 10^{18}$ cm^{-3}) is heavily p^+-doped ($2 \cdot 10^{20}$ cm^{-3}) using a zirconia-based diffusion source. Lowest ρ_c values obtained are smaller than $1 \cdot 10^{-6}$ Ω cm^2, which are among the best for p-contacts ever reported.

For low resistive ohmic contacts used in the fabrication of III/V semiconductor devices, highly doped p^+-layers are commonly demanded. They are most conveniently achieved by an acceptor diffusion. Due to its high diffusion coefficient and low ionization energy, zinc is most widely used for this purpose. Among the various diffusion techniques, solid-state diffusion has gained increased importance because of its superior handling performance, high flexibility with respect to short process times, and inherent protection of the semiconductor against thermal damage. In preceding papers,[1-3] the advantages of p^+-diffusion sources based on zinc-doped alumina and zirconia films have been described. It has been shown by means of secondary ion mass spectrometry and C-U-profiler measurements that (*i*) hole concentrations of up to $7 \cdot 10^{19}$ cm^{-3} (corresponding to $2 \cdot 10^{20}$ cm^{-3} for the concentration of Zn^{2+} in the topmost region) are obtainable and that (*ii*) the diffusion profile follows a typical complementary error function.

With this very high doping, excellent specific contact resistivities, ρ_c, defined as the area-specific resistances of the metal-semiconductor interface can be achieved. To obtain values of the contact resistivity, we have to consider the resistivity of small spots on a thin, highly conductive substrate. ρ_c can be obtained from experimental voltage drops when the specific resistivity of the substrate, ρ_0, and the contact area, F_c, are known. ρ_c is then expressed as function of the voltage drop U_0 caused by a current I_0 across the area of the ohmic metal-semiconductor interface. The main problem we have to deal with is the calculation of the current distribution.

An ideal contact does not exhibit any interfaces. In fact, practical contacts differ from that ideal behavior mainly due to (*i*) differences in the work functions of metal and semiconductor yielding potential barriers, (*ii*) surface states of the semiconductor, and (*iii*) poor adhesion.

In our novel technique, we made use of a direct ohmic measurement which avoids the assumptions necessary when applying the transmission line method (TLM).

Theory

The most commonly used technique for the determination of ρ_c is the TL method which is applied to a series of voltage pads differing in distance, s, but equal in area, $a = l \cdot w$, where l is the length parallel to the TL, and w the length perpendicular to it. For this arrangement, Berger[4] and Murmann and Widmann[5] solved the one-dimensional lossy transmission line equation (with zero metal sheet resistance) using the Helmholtz equation $\partial^2 V/\partial x^2 = V/l_t^2$ with $l_t = \sqrt{\rho_c/R_\square}$, a decay length which is commonly referred to as the transfer length, l_t indicates the average mean-free path of carriers in the semiconductor. The resulting resistance as a function of distance, s, usually gives a straight line. From its slope, the sheet resistance $R_\square$, divided by w, is obtained, and where the separation is zero the R-intercept is twice the contact resistance, R_c, and the s-intercept twice the

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