OHMIC CONTACTS ON p - GALLIUM PHOSPHIDE

By
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A b s t r a c t: The problem of making ohmic contacts on semiconductors is reviewed and a compilation of conditions for the formation of such contacts is attempted. A detailed study of a number of alloys for improved ohmic contacts of p-type GaP is presented. The alloys Au-Sn, Au-Sb and In-Zn wet GaP forming on it a shallow contact which is ohmic.

1. Introduction.

One of the main problems in semiconductor research and the technology of device fabrication is the formation of ohmic metal - semiconductor contacts of low resistance in order to avoid rectification anisotropy and spurious sources of e.m.f. that usually reside there.

The problem of ohmic metal to semiconductor contacts presents inherent difficulties and the realization of these contacts is more or less an empirical problem which does not depend on exact scientific reasoning, so that the solution refers always to a particular pair of materials. Nevertheless in approaching this problem one has to take in account several factors that may lead to non - ohmic contacts, although there is no assurance that the result will be satisfactory by avoiding them or taking all of them into consideration.

In forming a metal to semiconductor contact usually a double layer is formed with the surface becoming positively charged due to the formation of a depletion layer. As a result a potential barrier of height φ_B is formed which depends on the work function of the metal φ_M, the electron affinity of the semiconductor χ and finally the potential drop across the barrier Δ. Thus

$$\varphi_B = \varphi_M - \chi - \Delta \qquad (1)$$

This simple model suggests that if the work function of the metal is

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lower the chance of getting an ohmic contact is greater. Usually the height of the barrier for an ohmic contact should be 0,10 eV or smaller. Apart from the metal work function one should consider the correlation between the barrier height and the electronegativity values, which suggest that an important role must be attributed by the partially ionic nature of the semiconductor-metal bond.

Unfortunately the above stated equation is not applicable in most of the experiments, since even for an intimate contact, the work functions are not necessarily the vacuum values. Thus surface dipole contributions, surface states at the semiconductor - metal interface etc. modify the barrier height.

According to Bardeen at a surface state concentration $\gg 10^{13}$ cm^{-2} the barrier height becomes insensitive to the metal work function. Because of the usually employed techniques in making the diodes, the surface states are assumed to be in intimate contact with the semiconductor and hence are fast states. As pointed out by H. Gatos and M. Lavine [1] the nature of the etchant and the etching conditions have pronounced effects on the electrical properties of semiconductor surfaces. In general low values of surface recombination velocities are associated with high surface barriers. Surface treatment which tends to make the surface strongly p or n produces low surface recombination velocities.

Kröger, Diemer and Klusens [2] suggest that at the surface of the semiconductor adjacent to the electrode, there exists a thin exhaustion barrier through which electrons tunnel to reach a strongly conducting sublayer that acts as a supply of electrons for the remaining bulk. As long as the energy of the free electrons in the metal contact remains less than the exhaustion barrier peaks, the net carrier density that tunnels into the crystal is of the general form

$$N = \int_{E_1}^{E_2} [N_1(E) - N_2(E)]\Psi(E, x, A)dE \qquad (2)$$

where the function $\Psi(E, x, A)$ is the probability of tunneling, depending on the electron energy E, the barrier thickness x and the contact area A. $N_1(E)$ and $N_2(E)$ are the carrier densities of energy E in the metal and in the semiconductor conduction band respectively. The band model [3] for the contact is presented in figure 1. Thus the electrons in moving through the barrier into the high conduction regions, tunnel alternately via asymmetrical barrier thicknesses and the resulting V - I plot is diodic.

In several cases during contact formation an alloy is formed which

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deposits on the parent semiconductor material in such a way so that the lattice structure of the parent extends into the alloy phase. This regrown

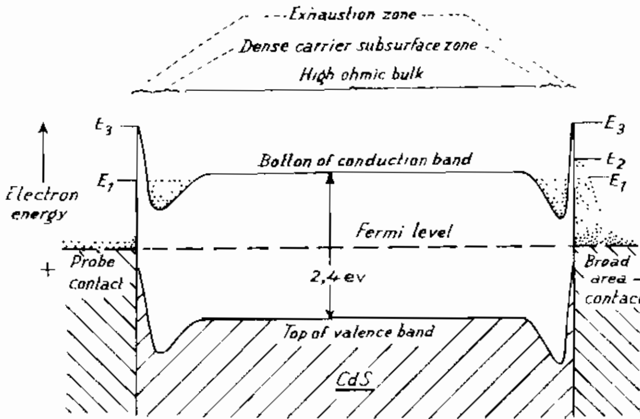

Fig. 1. Band model of the contact between CdS and a metal probe (left) and a broad area metal film (right).

region may be of opposite type (usually p - type), and being monocrystalline it forms a p - n junction. This situation is encountered in the case of aluminum contacts on silicon [4].

Apart from physical and chemical considerations one has to take in account the mechanical structure of the contact. Salkov and Sheinkman [5], investigating metal - semiconductor contacts, have found an abrupt increase of the photoresponse at the contacts, a characteristic of regions of increased resistance in the vicinity of the electrodes, although the potential drop did not show any noticeable jumps. The existence of this increase in the photoresponse proved that such regions should exist, but they may be so thin that in voltage probing they pass unnoticed. The above authors theorize that the regions of high resistance are due to inhomogeneous structure of the contact, which consists of a series of cusps and needle points so that the current lines of the electrode itself converge abruptly to separate parts of the electrode with small cross sections. Cusps at the contacts can be provided, for example, by dislocations which emerge at the surface of the crystal into which the metal diffuses.

2. Experimental realization of ohmic contacts.

As already pointed out the formation of an ohmic contact for a gi-

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ven semiconductor is an art. From the above considerations, the general thoughts that ought to guide one in forming a contact are the following:

i) Selection of a proper metal with a low work function compared to the electron affinity of the semiconductor.

ii) Elimination, if possible, of the surface states.

iii) Perforation of the surface barrier.

In step (i) the general practice is, instead of using a simple metal, to use an alloy of a metal with low work function, such as indium, with an element which is similar to the donor or acceptor impurities of the semiconductor. Thus a graded junction is formed referring to the impurity.

Elimination of the surface states is achieved using a reducing atmosphere during contact formation, such as hydrogen atmosphere or a suitable flux.

Metal - semiconductor contacts are formed by noble gas discharge prior to metal deposition. In this case the metal used for evaporation seems to be of no importance, the apparent source of conduction electrons being the highly disorded region at the surface due to the discharge.

Recently the formation of contacts through sequential evaporation or coevaporation of suitable metals has been proposed for CdS [6]. The choice of the preparative metal is determined by the desired reactions at the surface, which are:

a) Desorption of chemisorbed surface layers without damaging the surface or changing its stoichiometry (as in the case of gas discharge).

b) Chemical reaction with the chemisorbed active gases.

c) Chemical reaction with the compound that may be formed in step b.

In the case of CdS coevaporation of Ti and Al allows the formation of an ohmic contact under conditions in which Al alone forms blocking contacts. This can be explained by the getter action of the Ti,decreasing the partial oxygen pressure during evaporation, as well as by a chemical reaction of Ti with the oxide layer of Al_2O_3 formed on the surface.

Finally the contact should be treated in order to eliminate the surface barrier. Annealing the contact results in a more homogeneous contact area so that paths of high resistance are eliminated. The perforation of the barrier is facilitated by a current discharge through it. On applying high voltage at the probe, the Fermi level of the probe drops, so that the energy level E_2 sinks below the level E_1 (figure 1). If the difference is pronounced the electrons perforate the barrier, that is, destroy the a-

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tomic structure in the vicinity of the probe. The effective thickness of the barrier has thus been reduced. A momentary discharge of a capacitor produces such a current surge. The electrode formation, using a high current pulse, presents practical difficulties in selecting a pulse high enough for electrode formation, but low enough to avoid breakdown destruction in the form of thermal stress induced cracks. A more practical approach [7], which has been found rather valuable, is by a Tesla coil discharge at the electrodes formed. In most cases such a discharge is capable in reducing the barrier width to yield lower resistance contacts which are more or less ohmic.

In view of the above stated difficulties in forming ohmic contacts, we have attached to this present work an appendix of the most common semiconductors together with the metals and conditions of contact formation.

3. Ohmic contacts on GaP (Cd doped).

Several methods for making «ohmic contacts» (i.e. contacts with linear current - voltage characteristic) on GaP have been reported, but experience with these contacts has shown that they are unsatisfactory for many reasons. The temperatures required were either too high and an oxygen doping occured or too low and unsuitable for conductivity or Hall effect measurements.

As shown in the Appendix most workers use metals of low melting point (e.g. In, Ga, Sn) or alloys with low eutectic point for making ohmic contacts, being indifferent as to the selection of the group of the periodic table. In some cases the contact metal - semiconductor is obtained by sublimation of the metal in high vacuum chamber and condensation of the vapor on the surface of the semiconductor.

The clean surface, as much as the selection of the appropriate dissolving medium, is critical. In general fats or organic compounds should be removed with the help of hot or boiling dissolving medium as e.g. benzol or xylol.

The usual procedure is the following:

i) Mechanical grinding of the specimen with extra fine grain SiC (1000 mesh).

ii) Washing in distilled water and in a solution of aether and alcohol.

iii) Dipping in an etching solution for several minutes. Some acids or bases polish the surface of the semiconductor instead of etching it. These should be avoided.

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The most satisfactory etching solutions were

i) Aqua regia

ii) 10 % Br_2 dissolved in methyl alcohol.

After being etched for a few minutes the specimen was immersed in methyl alcohol to avoid surface contamination.

All the contacts were made by vacuum alloying using a Pt foil filament. By thermal radiation due to Pt foil, the temperature on the surface of the specimen supporting the alloying contacts was raised slowly, until the melting point of the alloy was reached. At the same time a small amount of hydrazine surrounding the specimen dissociated producing a reducing atmosphere. The pressure in the system at the beginning was typically of the order 1×10^{-5} Torr. The temperature was estimated with the aid of a thermocouple near the specimen. The specimen supporting the alloy in form of small grains (approximate diameter 0,5mm) at the appropriate places was heated until the grains were transformed into small balls and then they started alloying with the specimen. Two typical photographs of the procedure are seen below (fig. 2a, b).

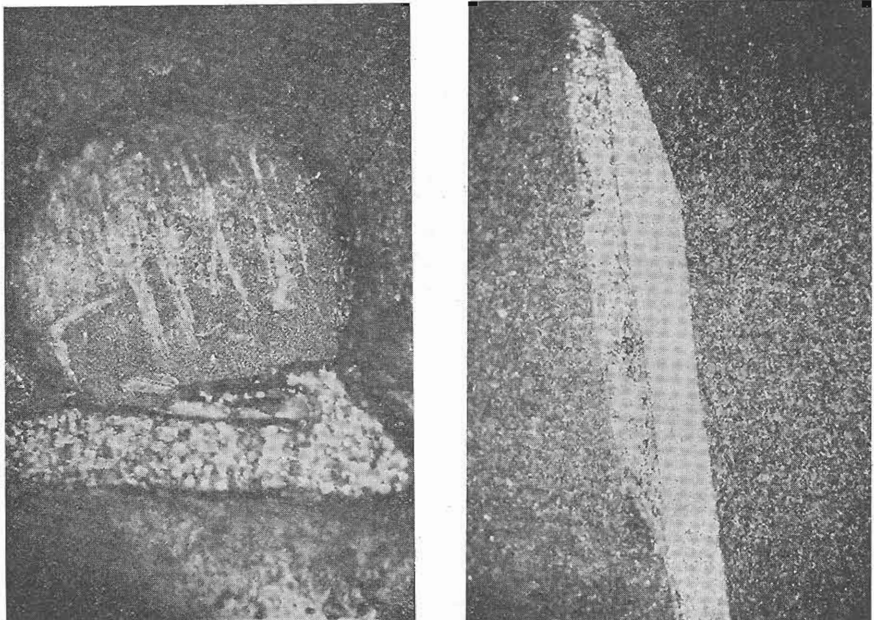

Fig. 2. Specimen supporting the metal grain, which has been transformed after heating (a) into a small ball and (b) into u shallow contact, due to alloying with the specimen.

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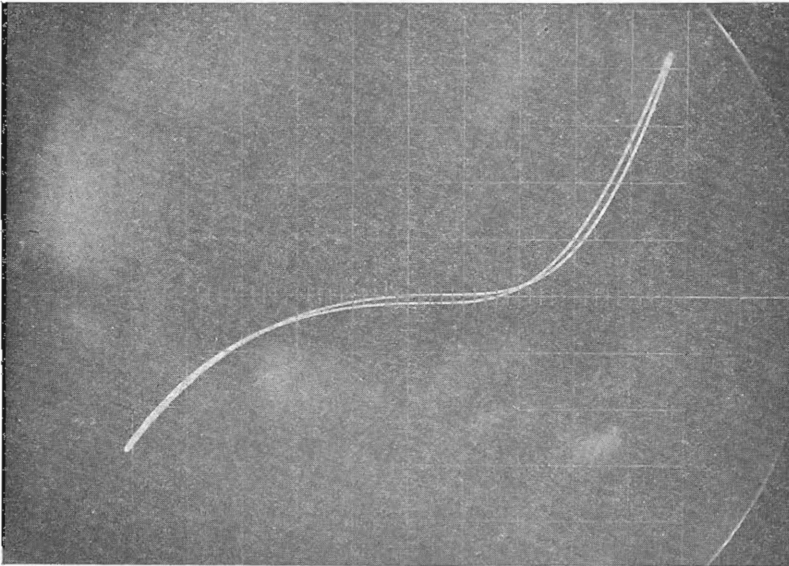

Fig. 3a

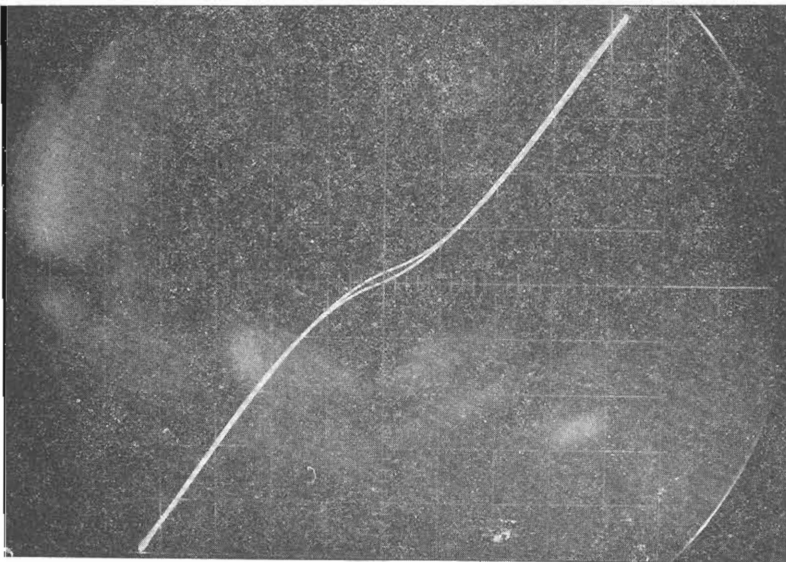

Fig. 3b

Fig. 3. Current-voltage characteristic for (a) non ohmic contact and (b) for ohmic contact.

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The following alloys were examined:

In - Zn (2.8 %)	(m.p. 143,5°C)
In - Sn (48 %)	(m.p. 117° C)
Sn - Zn (91 %)	(m.p. 198° C)
Cd - Ga (87 %)	(m.p. 258° C)
Cd - Sn (68 %)	(m.p. 177° C)
Cd - Sb (7 %)	(m.p. 290° C)
Cd - Zn (17.5 %)	(m.p. 266° C)
Au - Sb (25 %)	(m.p. 260° C)
Au - Sn (20 %)	(m.p. 280° C)

The ohmic behavior of the contacts was estimated

i. By the lowest possible value of the resistance.

ii. By measurement of current-voltage characteristic. As a voltage source the secondary of a low output impedance transformer was used. The I - V characteristic was almost a straight line (fig. 3b).

iii. By making two contacts of different effective areas we obtained an asymmetrical characteristic for non-ohmic constacts (fig. 3a), whereas in the case of ohmic contacts an almost straight line symmetrical characteristic.

It was found that the resistance of the contacts could be reduced either by discharging a capacitor through them or by a Tesla coil discharge.

All these investigations showed that the lowest value could be obtained by alloying the specimen with the following alloys.

i. Au - Sn (20 %)	(m.p. 280° C)
ii. Au - Sb (25 %)	(m.p. 360° C)
iii. In - Zn (2.8 %)	(m.p. 143.5° C)

with corresponding values for the specific resistance of the bulk of the order of 10^{-1} Ω.cm.

SUMMARY

The tbree kinds of alloy contacts reported here give repeatable and reliable ohmic electrical contacts on n-type GaP (Cd doped). These contacts can be made at relatively low temperatures, which are necessary if we are to avoid oxygen doping, but still high enough for electrical measurements in a wide range of temperatures.

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ACKNOWLEDGMENTS

We would like to thank Mr. D. Dario Schibe and A. Barbas for their help in the literature search and also the National Hellenic Research Foundation for its financial support.

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APPENDIX

No	*Material*	*Etchant*	*Appropriate metal for ohmic contact*	*Remarks*	*Reference*
1	$CdAs_2$		Sn		8
2	$Cd_xHg_{1-x}Te$		Ag-paste	Good electrical contacts are obtained by soldering them with silver paste in holes bored at the sample	9
3	CdS		In, Ga	A simple and convenient technique of applying electrodes is to evaporate an opaque layer of In to the crystal	10
	CdS		In, Ga		11
	CdS		Ti-(Ti-Al)-Pt	Multilayer method	6
	CdS		In or Al		12
	CdS		In	By evaporation of In, followed by short heating	13
4	n-CdSe		In	By evaporating In to the sample in vacuum	14
5	n-CdTe	1HF, $1HNO_3$, $2H_2O$, treated in a solution consisting of 7 parts saturated $K_2Cr_2O_7$ solution and 3 parts concetrated H_2SO_4	In		15
6	Cu_2O	Fresh cleaved surfaces	Sputtered platinum electrodes		16

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7	Cu_2S				13
8	n-GaAs		In doped with Te		17
	n-GaAs		Sn	Sn is welded to the GaAs at 400° to 450°C in vacuum (10^{-4}mmHg) for 5 min	18
	n-GaAs		In		19
	n-GaAs	$1H_2O$, $3H_2SO_4$, $1H_2O_2$ and then washing in de-ionized water	In	By alloying small pellets of In	20
9	p-GaAs		In doped with Zn		17
	p-GaAs		In	Via a deposited band of silver	19
10	GaP		Silver paste with a small admixture of Te		21
11	n-GaP	Boiling aqua regia	95%Au+5%Sn Alloy	Good ohmic contacts are created by using laser for welding	22
12	p-GaP	Aqua regia or 10% Br_2 in methanol	80%Au−20%Sn Alloy 75%Au+25%Sb Alloy 98.2%In+2.8%Zn Alloy		23
	p-GaP	Boiling aqua regia	95%In+5%Zn Alloy		22
13	GaS		In-Hg		24
14	n-GaSb		In	Ultrasonic soldering iron	25,49
15	$GdNbO_4$		Pt		26
16	n-Ge		Mo		27
	n-Ge		Cerroseal 35 solder	The surface is sandblasted and leads are attached with cerroseal 35 solder	28
	n-Ge		In		

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No	*Material*	*Etchant*	*Appropriate metal for ohmic contact*	*Remarks*	*Reference*
17	p-Ge		Cerroseal 35 solder	«Cerroseal 35 solder» consists mostly of tin with a small quantity of In. The sample is first cleaned with alcohol and then the solder put on using zinc chloride flux	30
	p-Ge	Hydrofluoric acid and cnpric nitrate	Rh		31
	p-Ge	CP4	In		32
18	GeTe	0.4N KOH	Au	Evaporation	33
19	HgCdTe		In		34
20	n-InAs	CP4 (47 sec)	In or Sn solder		35
21	InSb		In	By rubbing In and subsequently fusing In at 250 -300 C into holes of about 0.2 mm diameter drilled into the surface of the sample	36
	InSb		Ag	The contacts were silver-plated and soft soldered	37
22	n-InSb				38
23	$NdNbO_4$		Platinum	Platinum films are vacuum-deposited on the samples as contacts. Platinum wires welded to platinum blocks are used for electrical leads	26
24	n-Si	1HF, $1HNO_3$	Ge+Sb(1-2%) Alloy		39
	n-Si	Fum. HNO_3, conc. HF and glacial acetic acid	Al	By evaporation	4

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25	p-Si	1HF, $1HNO_3$	p-Ge or Ge with a weak n-type conductivity		39
	p-Si		Al		50
26	$SrTiO_3$	Mechanical polishing	In or Alloy of Zn-Cd-In	«Ultrasonic soldering iron»	40
	$SrTiO_3$	Mechanical polishing	In	«Ultrasonic soldering iron»	41
	$SrTiO_3$	Mechanical polishing	In or Mg		42
27	$Tl_2Se.As_2Te$	Mechanical polishing	Al	The electrodes are made of colloidal graphite, of Al deposited by evaporation in vacuum and of platinum wires fused directly into the sample	43
28	ZnS		In	Small pieces of In are placed on a ZnS crystal and heated for a few seconds at about 600° C	44
29	n-ZnS	Pyrophosphoric acid	In	By etching in hot (250°C) pyrophosphoric acid and immediately scribing on the contacts, with an In wire dipped in Hg. After adding more In to each contact they are fired in 350°C in H_2 atmosphere	45
30	ZnSe		In		46
31	$ZnSiP_2$	Samples were ground using special apparatus and fine carborundum powder	Pt	Platinum wires (50μ in diameter) welded to the sample by spark discharge were used as contacts	47
32	ZnTe		In		46
33	p-ZnTe	Hot concetrated NaOH	In	«Ultrasonic soldering iron»	48

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