IR 78 04 48

C.R.N.

centre de recherches nucléaires de Strasbourg

CRN-CNPA 78/27

MECHANISM OF FORMATION OF SCHOTTKY DIODES

J.P. PONPON, P. SIFFERT

CENTRE DE RECHERCHES NUCLÉAIRES

Groupe de Physique et Applications des Semiconducteurs

67037 STRASBOURG-CEDEX
(France)

Institut National de Physique Nucléaire et de Physique des Particules

Université Louis Pasteur de Strasbourg

IMPR. STRASBOURG-CEDEX FRANCE

MECHANISM OF FORMATION OF SCHOTTKY DIODES

J.P. PONPON, P. SIFFERT

CENTRE DE RECHERCHES NUCLEAIRES

Groupe de Physique et Applications des Semiconducteurs

67037 STRASBOURG-Cedex

(France)

ABSTRACT

The formation of the potential barrier at the metal-silicon contact has been investigated. Special emphazis was given to the study of ageing of gold-N type silicon Schottky diodes, showing that their electrical properties are directly correlated to oxygen diffusion through the metal. A phenomenological model based on the behaviour of oxygen with respect to the metal involved is proposed to describe the ageing for any metal deposited on N or P type silicon.

1. INTRODUCTION

The ageing of Schottky barriers has been observed years ago, especially when making silicon nuclear radiation detectors. However, although this problem was recognized to have a large influence on the properties of the devices, it has not been satisfactorily explained. For the special case of a gold contact on N-type silicon, which has been one of the most widely investigated, it is known that no rectification occurs after manufacturing as long as the device remains in vacuum. Only when air or oxygen is introduced, the reverse characteristic appears, so that the reverse current at a fixed voltage decreases as a function of time of exposure. These results lead SIFFERT et al [1] and BADER et al [2] to postulate that the rectification properties of Schottky barriers are strongly related to the diffusion of oxygen or water vapour from the ambiant through the metal layer. Thus, their conclusions were the following : first, after air or oxygen has been introduced for the first time on the vacuum deposited contact, oxygen diffuses through the gold film of thickness x according to the following relation :

$$x = \sqrt{6 D \tau} \quad , \tag{1}$$

where τ is the time needed by oxygen to cross the metal and D the diffusion coefficient. In fact, this relation describes the general law of gas diffusion through a membrane [3]. The temperature dependence of the process was found to be described by :

$$D = D_o \exp (- U/kT), \tag{2}$$

where k is the Boltzman constant, T the temperature, D_o a constant ($D_o \simeq 2.5$ cm^2/s) and U the activation energy, which was found to be close to 0.85 eV.

After a time delay τ, the reverse current for a given bias voltage decreased following the law :

$$I = a\, t^{-b}, \qquad (3)$$

where a is a constant and b varies from sample to sample, depending on the fabrication procedure, from 0.5 to 2.

From the point of view of the rectifying process at the metal (M) - semiconductor (S) contact such results cannot be explained by taking into account the difference between the work function of the metal and the semiconductor (Schottky theory) neither by surface states at the interface, as these theories suppose that the potential barrier is formed immediately after close contact is realized between the metal and the semiconductor. Due to a lack of techniques to investigate surface layers with higher sensitivity and depth resolution the above mentioned hypothesis could not be verified at that time.

Since new interest in the field of M-S and metal-thin insulator-semiconductor (MIS) devices has developped for applications to solar cells, the ageing and stability of these structures has to be considered again. This constitutes the goal of this work in which these problems, as well as the more fundamental point of potential barrier formation at the gold-silicon contact, have been investigated by making more detailed studies of the change in time of exposure to air of the electrical properties of the samples and by using new experimental facilities to determine the structure of the interfacial layer and its behaviour when exposed to air. Furthermore, the new theoretical developments of MIS

solar cells have been used and the results compared to experimental data when the device is illuminated. Some preliminary results obtained with other metals (aluminium, lead) will also be included. Finally, a phenomenological model describing the potential barrier formation and the ageing of Schottky barriers for any metal deposited on N- or P-type silicon will be proposed. This model is based on : - the role of oxygen, the accumulation of which has been undoubtly established at the gold-silicon interface.

- the heat of formation of the oxide of the metal considered. In metals having a low oxide heat of formation, oxygen diffuses easily through the metal layer ; a large dependence in time of exposure to air is observed. When this heat of formation is high, oxygen becomes chemically bonded, only minor diffusion through the layer will occur and small ageing effects appear.

II. EXPERIMENTAL TECHNIQUES

A. SAMPLE PREPARATION

N- and P-type silicon, 10 Ω.cm in resistivity was used. After etching of the samples in a (2HF: 3 HNO_3 : 3 CH_3 COOH) mixture followed by rinsing in deionized water and drying, the metal was evaporated by Joule effect under a residual pressure of about 10^{-6} torr at a rate slower than 5 Å/s. Sometimes, a short etching in diluted HF (1 : 1) was employed prior to evaporation.

The contact thickness was monitored during deposition by using a quartz balance. The errors on the deposited thickness was always below 10%, as verified by the Rutherford backscattering technique.

The ohmic contact was made prior to the front contact preparation.

B. ELECTRICAL MEASUREMENTS

I-V characteristics were recorded under vacuum and during ageing,

both in dark and under tungsten lamp illumination (100 mW/cm^2).

The barrier height was determined both by the measurement of the saturation current and by the photoresponse (Fowler plot). Furthermore, the open circuit voltage V_{oc} under illumination is related to the barrier height ϕ_B in Schottky's model by :

$$V_{oc} = n\,(\phi_B - C), \qquad (4)$$

where C is a constant and n is the ideality factor of the diode. Then, provided that n does not change and that the device behaves following the thermoionic theory, one can obtain informations on ϕ_B by measuring only V_{oc}.

C. CHARACTERIZATION OF THE INTERFACE

The oxygen distribution at the interface was investigated by a combination of three techniques using ion beams, which have been described in detail elsewhere [4] :

- the relative depth distribution of oxygen (O^-) was determined by using secondary ions mass spectroscopy (SIMS) profiling ;

- the absolute oxygen concentration at the interface as well as at the free silicon surface was measured by using the $^{16}O(\alpha, \alpha')^{16}O$ elastic scattering resonance (3,05 MeV) in channelling conditions and with the target held at low temperature;

- the depth scale of the SIMS spectra was obtained by 1 MeV $^4He^+$ Rutherford backscattering experiments at an optimized low angle geometry (glancing incidence). Such studies have been performed on the gold-silicon devices as a function of metal thickness and time spent in air before the measurements. For the other metals, only qualitative experiments have been done.

III. RESULTS

A. GOLD ON N-TYPE SILICON

1. Electrical properties

- DARK I-V CHARACTERISTICS

Since such characteristics have been widely studied by the authors of refs. [1-2], we shall restrict ourselves to report a typical example. Fig. 1 illustrates the behaviour of a device having a 300 Å thick gold electrode. It appears, in agreement with the earlier work, that, as long as the sample remains under vacuum after manufacturing, no rectification occurs (curve 1). When air is introduced at time t = 0, the curve does not change for a few minutes (at 300°K) corresponding to the time defined as τ in eq. 1 (curve 2). Then, the reverse current at a fixed voltage decreases following eq. 3., again in agreement with the authors' earlier investigations.

- I-V CHARACTERISTICS UNDER ILLUMINATION

The former characteristics have also been plotted when the sample was illuminated. The results are reported in fig. 2a and 2b : under vacuum (curve 1, fig. 2a) the characteristic is nearly the same as in the dark(curve 1, fig. 1) and practically no photovoltage is delivered. After air has been introduced, as the rectification occurs, the photovoltage V_{oc} starts to increase following a delay dependent upon the gold thickness. Typical characteristics of the cell under illumination are reported (fig. 2a, curves 3-6 ; fig. 2b, curves 1-2). V_{oc} increases following a logarithmic rate up to its saturation value. For gold, the later is about 0.3 V. For a longer exposure to air, the I-V characteristics are modified so that reduction of the photovoltaïc current is observed : the M-S structure becomes a MIS cell with a too thick interfacial layer (fig. 2a, curves 4-6).

- INFLUENCE OF HUMIDITY ON V_{oc}

We have compared the evolution of the photovoltage of a 100 Å thick gold layer on N-type silicon as a function of time of exposure to air whose relative humidity was 30 % and 90 %. It appears that the saturation value of V_{oc} is the same, however the time necessary to reach this plateau is very different : about 30 min. in wet air and 3, 000 min. in dry air.

- BARRIER HEIGHT

The forward current-voltage characteristics in the dark for low applied bias as a function of time of exposure to air, are reported in Fig. 3, for a 700 Å thick gold electrode structure. It appears that the forward and saturation currents are reduced by orders of magnitude during this evolution, while the factor n remains practically unchanged. We observed that, within the experimental error (about 0, 02 eV), the barrier heights measured by this procedure are in good agreement with photoresponse results. The evolution of ϕ_{Bn} for devices having gold electrode thicknesses ranging from 100 to 1100 Å is reported in Fig. 4. After manufacturing, ϕ^i_{Bn} has a rather low value ($0.5 < \phi^i_B < 0.6$ eV), which depends upon the surface conditions after cleaning. After a time delay $t_\phi(x)$, which varies with the electrode thickness, ϕ_{Bn} increases following a logarithmic dependence versus the time of exposure to air up to a value (ϕ^f_B) close to the barrier height (0, 8 eV), generally indicated in the literature for this contact (which is reached at the time $t'_\phi(x)$).

2. Oxygen distribution at the interface

The distribution profile of oxygen at the gold-silicon interface has been measured as a function of time of exposure to air. A typical O^- SIMS profile

for a 100 Å thick gold layer deposited on silicon is shown in fig. 5, together with Si^- and Au^- after ageing of the diode. It appears that :

- oxygen accumulation at the interface is clearly seen ;

- in agreement with other SIMS measurements, the shape of the Au^- and Si^- curves is dependent upon the oxygen concentration, due to the enhanced sputtering rate of the species in presence of oxygen ;

- no evidence of silicon diffusion towards the metal surface is observed for this sample prepared at room temperature. This has further been confirmed by RBS measurements.

The evolution of the oxygen concentration below a 100 Å gold electrode as a function of time of exposure to air is shown in fig. 6.

The concentration peak is linear (concentration of O^- proportional to peak area) and the origin of the depth scale coïncides with the gold surface. The change of the oxygen accumulation at the interface $\Delta [O]$, defined as the difference between the oxygen amount below the gold layer at time t : $[O]$ and the oxygen amount at the free silicon surface just after cleaning : $[O]_S$, has been plotted in fig. 7 both for 100 and 400 Å thick gold layers. $[O]_S$ has been evaluated, through the nuclear resonance measurement, to be 2.4×10^{15} cm^{-2} and equal at t = 0 to $[O]$: therefore, at t = 0, $\Delta [O] = 0$. After the samples are removed from vacuum $\Delta[O]$ remains equal to zero up to a time t_o (which is about 200 s. for the thin electrode and 3200 s. for the thicker one) then it increases following a logarithmic law at a rate of about $1.2 \times 10^{15} cm^{-2}$ per time decade over more than five decade This evolution at the free silicon surface is only of 2.7×10^{14} cm^{-2} per time decade.

These results demonstrate that oxygen (or water vapour) from the ambiant diffuses through the gold layer and accumulates at the gold silicon interface. In addition, the presence of gold increases the process of oxygen adsorption and / or of oxidation of silicon.

Quite similar results have been observed on P-type silicon, however, the experiments have been less reproductible. In summary, the oxygen accumulation below the gold layer can be described by the following relation :

$$\Delta [O] = 0 \qquad \text{for } t < t_o$$

$$\Delta [O] = K \ln (t/t_o(x)) \quad \text{for } t \geq t_o , \qquad (5)$$

where K is a constant (close to 5×10^{14} cm^{-2}) and $t_o(x)$ is the time needed by O^- (or OH^-) to cross the gold layer of thickness x.

B. LEAD ON P-TYPE SILICON

To investigate the ageing of Schottky diodes on P-type silicon and in order to verify some of the assumptions we shall discuss later, we thought that it could be usefull to study the properties of a contact made with a metal having a minor tendency to oxidize. Lead was choosen, since, for the metals producing rectifying contacts on P-type substrates, it is the one with the lower heat of formation of oxides.

1. Electrical properties

- DARK I-V CHARACTERISTICS

The current-voltage characteristics for a 300 Å thick lead contact on P-type silicon are reported in fig. 8. Under vacuum (curve 1) rectification occurs but with a rather high leakage current. When air is introduced not only the reverse but also the forward current rapidly decrease (curves 2-3).

-I-V CHARACTERISTICS UNDER ILLUMINATION

As also shown in fig. 8, the typical solar cell characteristics appear in vacuum with a rather high series resistance (curve 1) ; the open circuit voltage is quite large (V_{oc} = 0.33 V), always higher than the values reported after ageing for gold contacts on N-type material. This indicates that the barrier height ϕ_{Bp} is larger than expected from the literature (0.55 eV) [5] ; from the saturation current measurements, we deduced under vacuum a value of ϕ_{Bp} = 0.73 eV.

In air, a change in the shape of the I-V characteristics arises in a few minutes (curves 2-3), indicating that a MIS device with a thick interfacial layer is formed. At the same time, V_{oc} decreases in approximately 100 min. down to about half its original value in vacuum.

2. Oxygen distribution

Accumulation of oxygen at the lead silicon interface was observed qualitatively by SIMS. Fig. 9 shows on a log. scale the distribution profiles of Pb^-, O^- and Si^- for a sample having a 300 Å thick electrode after one day of ageing. At the interface, the amount of oxygen is very high and large quantities of oxygen are also present within the metallic film. Diffusion of oxygen through a lead layer seems to proceed at a very high rate, which could be due to a porous structure of the layer ; oxidation of the layer takes place simultaneously.

C. ALUMINIUM ON P-TYPE SILICON

Aluminium is a widely used metal in semiconductor technology. It gives a rectifying contact on P-type silicon, due to its low work function and in addition it is easily oxidized when in thin layers.

1. Electrical properties

We investigated only the behaviour of the I-V characteristics in air under illumination. Under vacuum, immediately after manufacturing the device, rectification occurs. Photovoltaïc voltage and current are delivered (V_{oc} = 0.26 V). When exposed to air no significant change is observed over long periods of time, provided the aluminium layer exceeds about 100 Å.

2. Oxygen distribution

The Al^-, Si^- and O^- distributions for a 300 Å thick aluminium layer on silicon are shown in fig. 10a. Contrarily to the previously considered gold and lead films, no accumulation of oxygen is seen, this element is distributed through the metal. This constitutes a typical result for an easily oxidized metal : as oxygen immediately reacts with the metal it is not available for diffusing at the interface. Further, when the aluminium layer is thick enough it will hinder any further diffusion of oxygen at room temperature. It is, however, interesting to notice that oxygen accumulation is even possible at the aluminium-silicon interface, when the metal layer is below 100 Å in thickness, as demonstrated by fig. 10b. This result has to be related to the rectifying properties of thin aluminium layers on N-type silicon after a long time of exposure to air, we observed years ago.

IV. DISCUSSION

The experimental results presented above have shown that, when oxygen accumulates at the metal-silicon interface, a large time dependence of the electrical properties results, independently of the type of the base material. The oxygen accumulation produces an increase of the potential barrier in N-type silicon and a decrease in P-type.

Three main problems have to be discussed at this point : what is the correlation between the evolution of $\Delta[0]$ and ϕ_{Bn} in the case of gold contacts ; what is the effect of the metal on the time dependence and, finally, what is the origin of the observed time dependence.

A. TIME DEPENDENCE OF BARRIER HEIGHT AND OXYGEN ACCUMULATION FOR GOLD-N-TYPE SILICON CONTACTS

– initial period up to $t_o(x)$: it is reasonable to assume that the time $t_o(x)$ needed by oxygen to cross the gold layer corresponds to the delay $t_\phi(x)$ we observed before the barrier height begins to increase. This time should be the same as that τ, defined in eq. (1), before the leakage current at a fixed voltage starts to decrease. These assumptionshave been verified in Table I for various film thicknesses x.

Within the experimental errors, excellent agreement is observed between $t_o(x)$, $t_\phi(x)$ and τ when assuming, for calculating the later, that $D = 8.4\,10^{-16}\,cm^2/s$ (300°K). This value is within the limits of error that BADER et al [2] have reported. Consequently, it becomes possible to determine t_o for any film thickness x.

TABLE I

Gold thickness (x) Å	τ (x) (s) (calculated)	t_o (x) (s)	$t_\phi(x)$ (s)
100	2.0×10^2	2.0×10^2	$< 2 \times 10^2$
300	1.8×10^3		3×10^3
400	3.2×10^3	3.2×10^3	
700	9.7×10^3		6×10^3
1100	2.4×10^4		10^4

- evolution after $t_o(x)$

As it appears in fig. 7, after the time delay $t_o(x)$, the growth of Δ [O] proceeds at a logarithmic rate and it is not very dependent upon the gold layer thickness. This logarithmic law can be explained by considering the theoretical model of metal oxidation proposed by RITCHIE [6] assuming that the rate determing step is oxygen ionization (it can be noticed that the room temperature oxidation of the silicon surface has been found to agree very well with this theory [7]). By using relations (1) and (5) , it is possible to build the full evolution curve of Δ [O] for any thickness x. On the other hand, it is possible to determine from fig. 4 the time $t'_{\phi}(x)$ for which the final barrier height ϕ^f_B is reached. By reporting this time on the built curve, the corresponding quantity Δ_{ϕ} [O] ban be evaluated for the various thicknesses used. Within a factor of two the oxygen coverage is the same when the barrier is established, independently of the metal thickness.

B. INFLUENCE OF THE METAL ON AGEING

The dependence of the ageing with the nature of the metal can be explained, at least from a qualitative point of view, by considering the heat of formation ΔH_o of the oxide of the contacting metal. For gold this value is - 2 kcal/mole, while it is equal to - 66 and - 404 kcal/mole, respectively for lead and aluminium. Then, when oxygen does not react easily with the metal, it can diffuse through it and a large dependence of the electrical properties with time of exposure appears. On the other hand, when a strong reaction between oxygen and the metal occurs, diffusion of oxygen is difficult. It can be noticed that for silicon ΔH_o = -210 kcal/mole, therefore,a metal like aluminium can react with the native silicon oxide by reducing it or by making a complex, then producing an interfacial layer whose properties are quite different from those of the native oxide layer after a gold deposition. Gold and aluminium really represent the extreme situation for which no competition between diffusion and oxidation

occurs. For most of the other metals these two processes are in competition and it is necessary to determine both the oxidation rate of a thin film and the diffusion constant of oxygen in it, to be able to evaluate the time delay after which ageing will occur. For example, it has been shown by SIFFERT et al [1] for more than 30 metals deposited on N-type etched silicon that after one year of ageing all the contacts were rectifying.

C. ORIGIN OF THE TIME DEPENDENCE

In a previous paper [8] we have demonstrated, by fitting I-V characteristics under illumination of gold on N-type silicon devices with the theoretical model of VIKTOROVITCH et al [9, 10], that this barrier can be described as a MIS structure with an interfacial layer of thickness $\delta = 5$ Å. In addition, it was shown that the lowering of the barrier height was due to a fixed positive charge situated in the native oxide layer. The assumption of such a positive charge is supported by recent experimental work on the structure of the silicon-silicon oxide interface [11-13], which demonstrated that a lack of oxygen exists in the oxide a few angstrom away from the silicon interface. Therefore, unsatisfied silicon bonds are present and lead to the existence of a positive charge. Immediately after manufacturing, when the device is still in vacuum, this charge has to be estimated to about 10^{13} cm^{-2}. When air is brought in contact it decreases as a function of time by one order of magnitude and ϕ_B^f is reached. By considering fig. 2b (curve 2), which corresponds to this case, it is seen that this situation is reached after about 5.10^5 s. This value is consistent with $t_{1/\phi}$ deduced from fig. 4 for a 300 Å gold layer. Thus oxygen has neutralized about 10^{13} cm^{-2} positive charges, which is orders of magnitude less than the total amount of oxygen available at the interface ($> 2.10^{15}$ cm^{-2}). This is probably due to the existence at the interface of an electrochemical equilibrium between

oxygen and the positively charged defects [6].

The assumption of the existence of a positive charge at the interface also explains the higher barrier height we observed on P-type silicon as long as the sample is in vacuum and the barrier height decrease during ageing. From a practical point of view, it has to be pointed out, especially for gold-Schottky barriers, that ageing can be strongly modified, depending on the chemical treatment used. Especially, when large quantities of negative ions, such as bromine or iodine, are present in the etching, they can neutralize the positive charges without the help of oxygen. This is in agreement with some empirical receipts used, even in industry, which indicate that halogens introduced in the etching or afterwards lead to stable diodes.

V. TENTATIVE MODEL

It is now possible to propose a qualitative model which takes into account the experimental findings. This model should include the heat of formation ΔH_o of the metal oxide as well as the metal work function ϕ_m. Four cases may be considered, depending on the values of these parameters.

1. Metals with high ϕ_m and low ΔH_o

The example investigated is gold on N-type silicon, but metals like platinum, silver, palladium, copper and nickel should behave in the same way.

After manufacturing, as long as the device is kept in vacuum, the fixed positive charge, located in the native oxide, reduces the barrier height to an initial value ϕ_B^i. In air, oxygen or water vapour diffuses through the metal layer as ions and reaches the interface after a time delay $t_o(x)$ depending upon the metal thickness and temperature, according to the general law of diffusion of a

gas through a membrane, given by eq. (1). Up to this time, no change in the electrical properties of the samples occurs. Then oxygen begins to accumulate at the interface and saturates the free silicon bonds of the native oxide. Due to the neutralization of this positive charge, the barrier height increases up to the final value ϕ_B^f, reached at the time $t_\phi(x)$. This barrier height corresponds to the value generally found in the literature. At this time, the oxygen accumulation $\Delta[O]$ is approximately the same irrelevant of the metal thickness x. Fig. 11 schematically shows the different steps of this process.

2. Metals with high ϕ_m and high ΔH_o

In principle, no metal can really fullfill these conditions. However, chromium can be considered in this group, since ΔH_o = -270 kcal/mole and rectifying contacts can be achieved on N- and P-type silicon. Such metals will reduce the native oxide layer and form a complex interfacial layer, in which no positive charge remains and, then no change occurs during ageing in air.

3. Metals with low ϕ_m and low ΔH_o

As in the former case, such a situation cannot exist ideally, only a metal like lead fullfills a part of these conditions. For an ideal case on P-type silicon, the positive charge in the oxide will increase the barrier height when the metal is deposited in vacuum. After exposure to air, the ageing proceeds in the same way as in case 1, leading here to a decrease of the barrier height, until the value from literature is reached.

4. Metals with low ϕ_m and high ΔH_o

Typical examples of this case are metals like aluminium, titanium or tantalum, which produce a rectifying contact on P-type silicon, provided the film is thick enough. As in case 2, reaction with the silicon oxide layer is

expected to occur during fabrication [14] but, as a strong reaction with oxygen happens when put in contact with air, no ageing will be present.

In practice, only cases 1 and 4 can be rather easily verified. For cases 2-3 and more generally for metals with medium values of ΔH_o (from -40 to -300 kcal/mole) ageing will occur but it cannot be described by a simple oxygen diffusion.

In addition, a few remarks can be made :

- Thin aluminium layers ($x < 100$ Å) are known to produce rectifying contacts on N-type silicon [15]. The same effect is expected for other group 4 metals. It would be due to the formation of a MIS or MOS structure.
- For metals from group 1 it will be difficult to obtain ohmic contacts on P-type silicon.
- The ageing effect will be strongly reduced, as pointed out above by using chemical etching having negative charges (bromine, iodine...) which are able to neutralize the positively charged surface. However, the diffusion of oxygen will not be hindered, but the dependence of the electrical properties upon time of exposure to air will be reduced.

VI. CONCLUSION

New results on the ageing of surface barriers have been obtained by combining electrical measurements and surface analysis techniques using ion beams. In contrast to the theories of rectification at the metal-semiconductor contact (Schottky theory or Bardeen theory) they demonstrate the large influence of oxygen and of its reaction with the contacting metal. A model allowing to explain, at least qualitatively, the ageing effects reported for many years in the literature has been proposed. Quantitative agreement has been obtained for gold and aluminium. For most of the metals however, a more precise description of the ageing will require a better knowledge of the diffusion of oxygen and oxidation process in thin metallic films.

REFERENCES

1. P. SIFFERT and A. COCHE, IEEE Trans. Nucl. Sci NS 11 (1964) n° 3, 244 also Le Vide special issue A.V.I.S.EM, october 1966, p. 140.
2. R. BADER and S. KALBITZER, Z. Naturforschg. 21 a (1966) 1072.
3. W. JOST, Diffusion Solids, Liquids and Gases, Academic Press Inc. Publishers, New York 1952.
4. J.P. PONPON, J.J. GROB, A. GROB, R. STUCK, P. SIFFERT, Third Int. Conf. on Ion beam analysis, Washington D.C. (1977) to be published in Nucl. Instr. and Methods.
5. B.L. SMITH and E.H. RHODERICK, Solid State Electron. 14 (1971) 71.
6. I.M. RITCHIE, Phil. Mag. 19 (1969) 421.
7. F. LUKES, Surface Science 30 (1972) 91.
8. P. VIKTOROVITCH, J.P. PONPON, Submitted to revue de Physique Appliquée.
9. P. VIKTOROVITCH, G. KAMARINOS, P. EVEN, C.R. Acad. Sciences, Paris 283 B(1976) 119.
10. P. VIKTOROVITCH, G. KAMARINOS, Journal of Appl. Phys. 48 (1977) 3060.
11. B.E. DEAL, J. Electrochem. Soc. 121 (1974) 198.
12. W.L. HARRINGTON, R.E. HONIG, A.M. GOODMAN and R. WILLIAMS, Appl. Phys. Lett. 27 (1975) 644.
13. R.A. CLARKE, R.L. TAPPING, M.A. HOPPER and L. YOUNG, J. Electrochem. Soc. 122 (1975) 1347.
14. A.G. REVESZ and T.D. KIRKENDALL, J. Electrochem. Soc. 123 (1976) 1513.
15. P. SIFFERT and A. COCHE, IEEE Trans. Nucl. Sci. NS 12 (1965) 284.

FIGURE CAPTIONS

Fig. 1 Evolution with time of exposure to air of the dark current-voltage characteristics for 300 Å gold on N-type silicon.

Fig. 2a Evolution with time (up to 120 minutes of exposure to air) of the current-voltage characteristics under illumination for 300 Å gold on N-type silicon.

Fig. 2b Evolution for longer times of exposure to air of the characteristics of the sample of fig. 2a. The optimum (curve 2) is reached after about $4.3\ 10^5$ seconds.

Fig. 3 Evolution with time of exposure to air of the dark forward characteristic and of the saturation current for 700 Å gold on N-type silicon.

Fig. 4 Evolution with time of exposure to air of the barrier height as deduced from the photoresponse and the saturation current for gold N type silicon samples.

Fig. 5 SIMS profiles of oxygen, gold and silicon ions for 100 Å gold on silicon.

Fig. 6 Evolution with time of exposure to air of the oxygen distribution in a 100 Å gold on silicon contact. Absolute calibration of the depth scale was made by Rutherford backscattering experiments.

Fig. 7 Evolution with time of exposure to air of the accumulation of oxygen $\Delta[O]$ at the gold-silicon interface. For 100 Å gold the time to is about 200 sec. while for 400 Å it is about 3200 sec.

Fig. 8 Evolution with time of exposure to air of the current-voltage characteristics for 300 Å Pb on P-type silicon. Both the characteristics in the dark and under illumination are shown.

Fig. 9 SIMS profiles of oxygen, lead and silicon ions for 300 Å lead on silicon. Note the large amount of oxygen in the metal layer as compared to fig. 5.

Fig. 10a SIMS profiles of oxygen, aluminium and silicon for a thick (300 Å) aluminium layer on silicon. No accumulation of oxygen is seen at the interface, but oxygen is entirely distributed in the metal.

Fig. 10b SIMS profiles of oxygen aluminium and silicon for a thin (100 Å) aluminium layer on silicon. Although a large amount of oxygen is seen in the first metal layers accumulation at the interface is observed, in contrast to the case of fig. 10a.

Fig. 11 Schematic model for the ageing of Schottky diodes made on N-type silicon with a high work function metal having a low oxide heat of formation. The upper curve shows the evolution with time of exposure to air of the oxygen accumulation at the interface for two metal thicknesses x_1 and x_2. The lower curve shows at the same time the evolution of the barrier height ϕ_{Bn}.

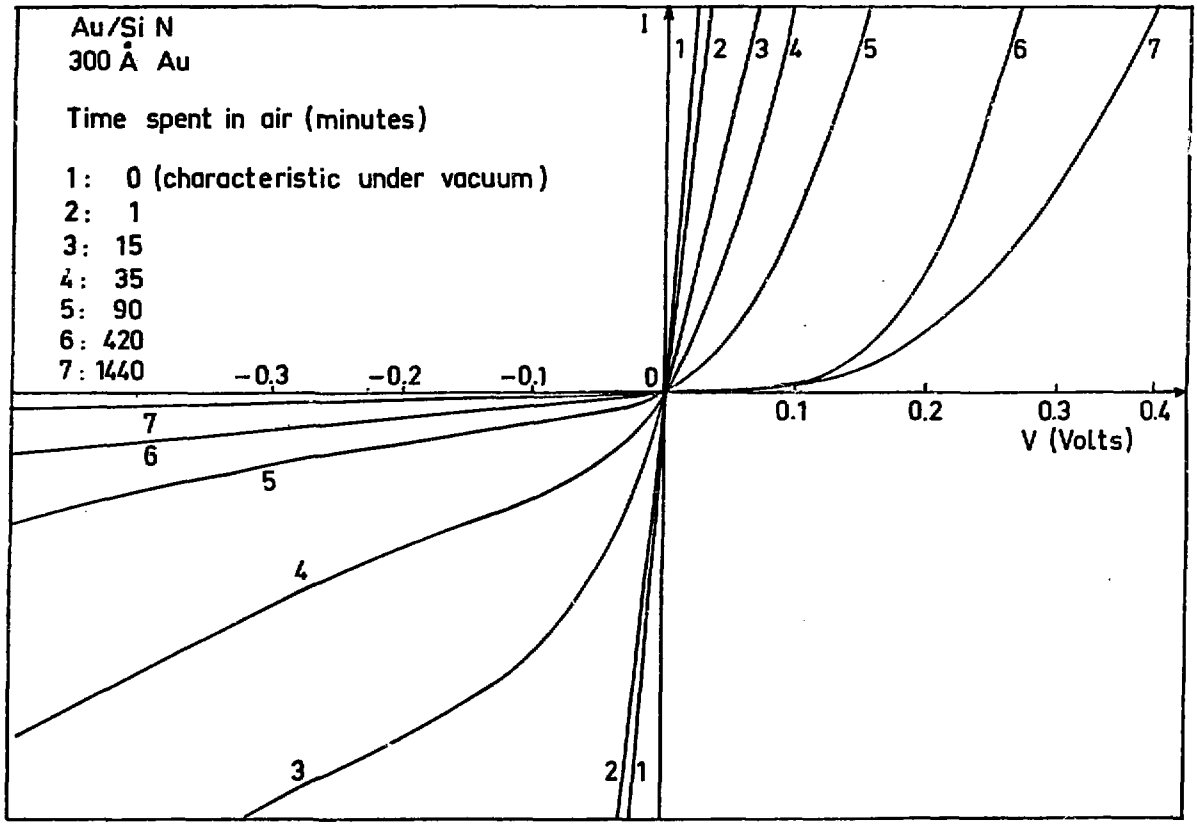
Au/Si N
300 Å Au
Time spent in air (minutes)
1: 0 (characteristic under vacuum)
2: 1
3: 15
4: 35
5: 90
6: 420
7: 1440
I
V (Volts)
−0,3
−0,2
−0,1
0
0.1
0.2
0.3
0.4

Fig. 1

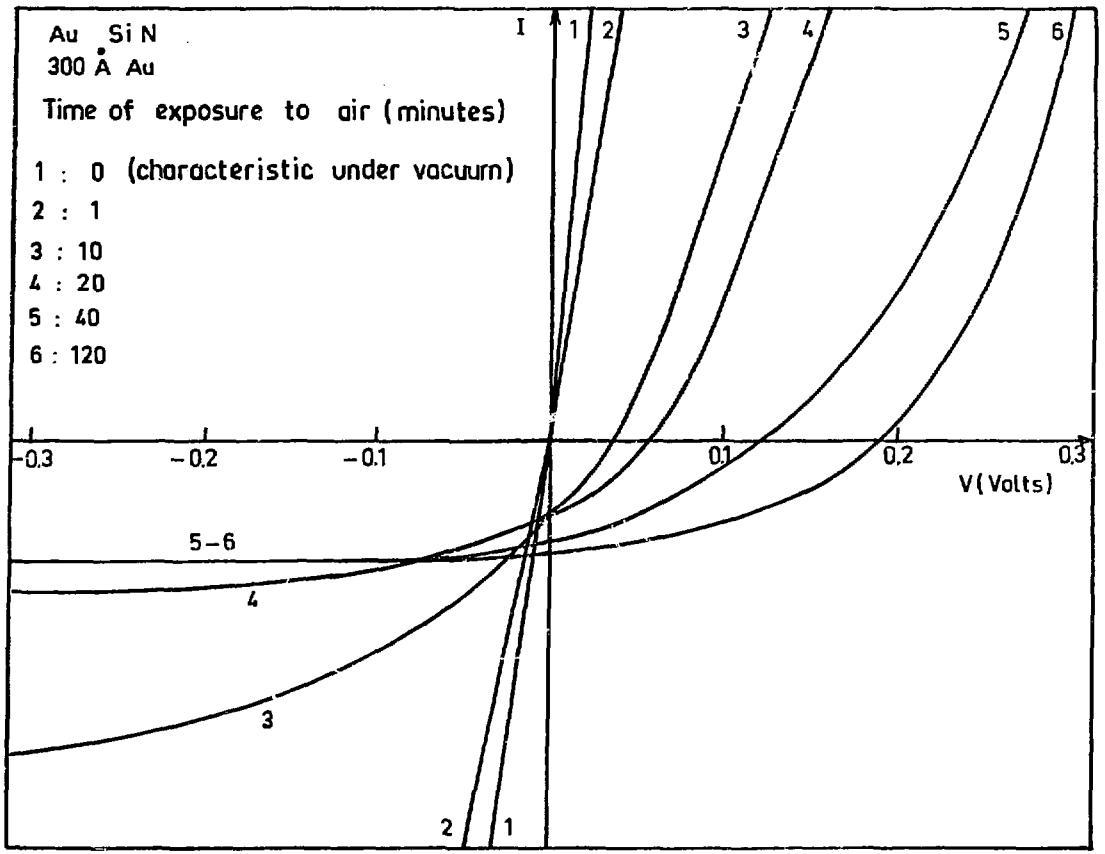
Au Si N
300 Å Au
Time of exposure to air (minutes)
1 : 0 (characteristic under vacuum)
2 : 1
3 : 10
4 : 20
5 : 40
6 : 120
I
1
2
3
4
5
6
-0.3
-0.2
-0.1
0.1
0.2
0.3
V (Volts)
5-6
4
3
2
1

Fig. 2a

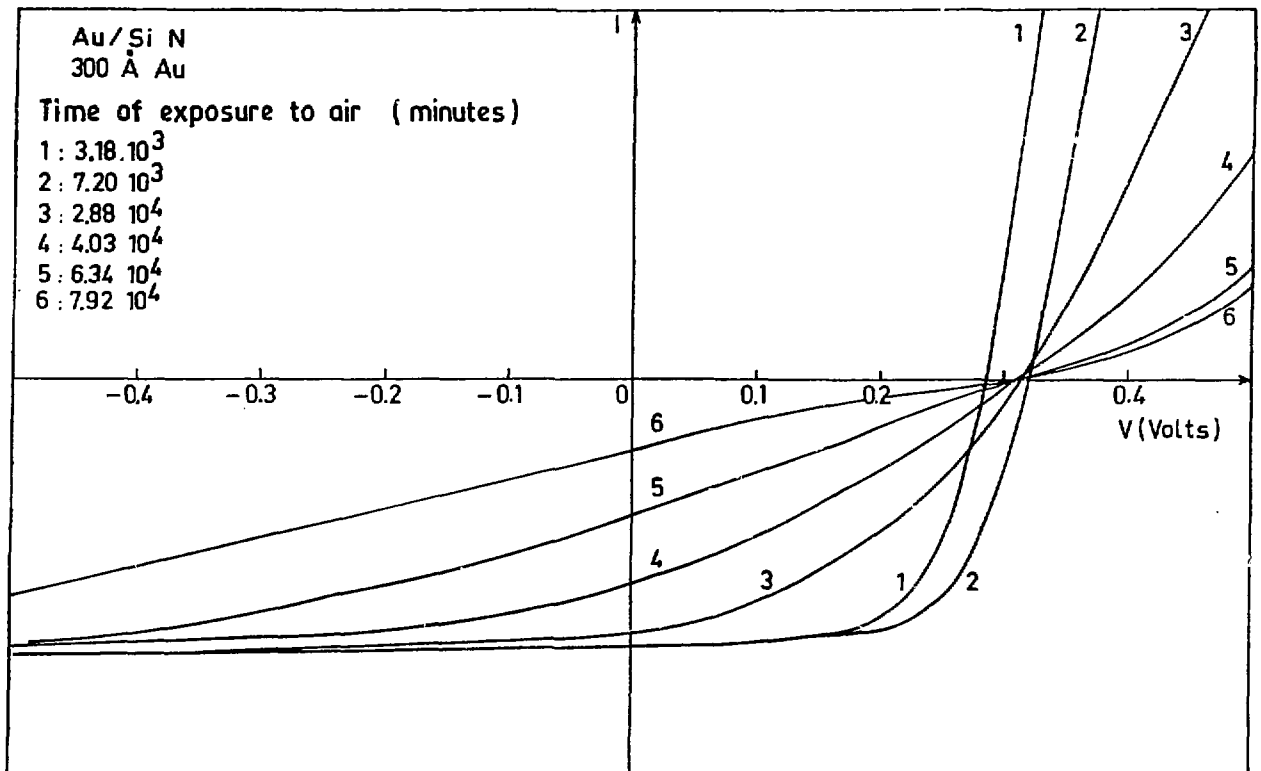
Au/Si N
300 Å Au
Time of exposure to air (minutes)
1 : 3.18.10^3
2 : 7.20 10^3
3 : 2.88 10^4
4 : 4.03 10^4
5 : 6.34 10^4
6 : 7.92 10^4
I
V (Volts)
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.4
1
2
3
4
5
6

Fig. 2 b

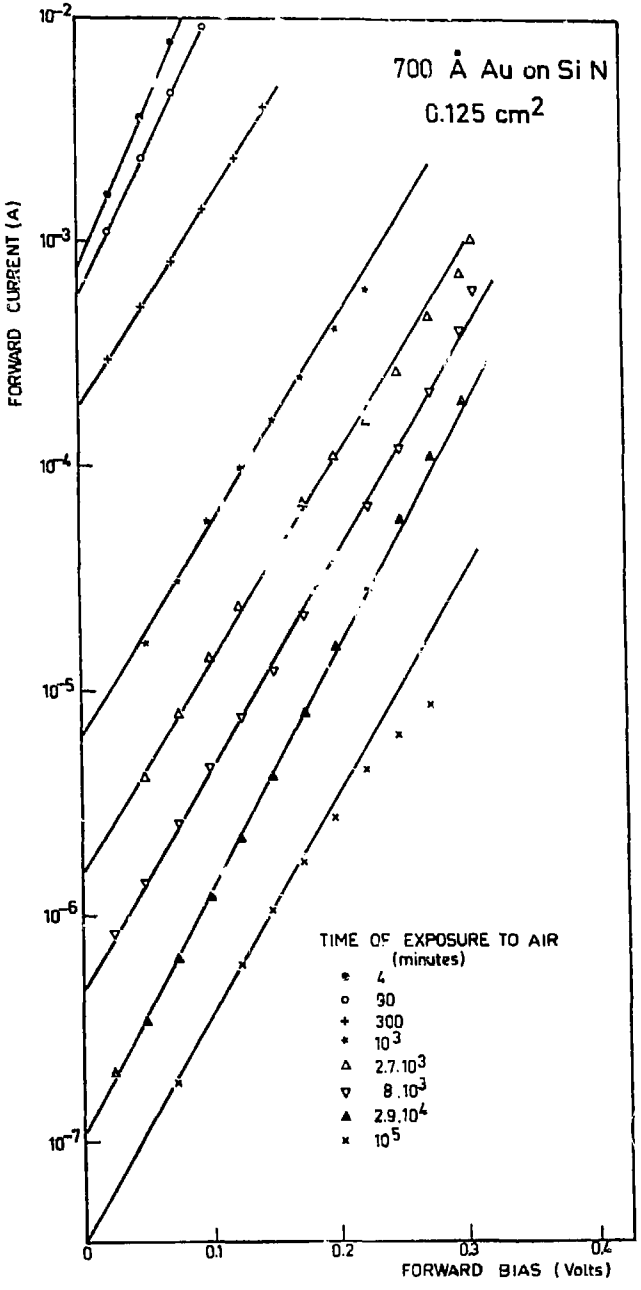
700 Å Au on Si N
0.125 cm²
FORWARD CURRENT (A)
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
0
0.1
0.2
0.3
0.4
FORWARD BIAS (Volts)
TIME OF EXPOSURE TO AIR
(minutes)
4
30
300
10³
2.7.10³
8.10³
2.9.10⁴
10⁵

Fig. 3

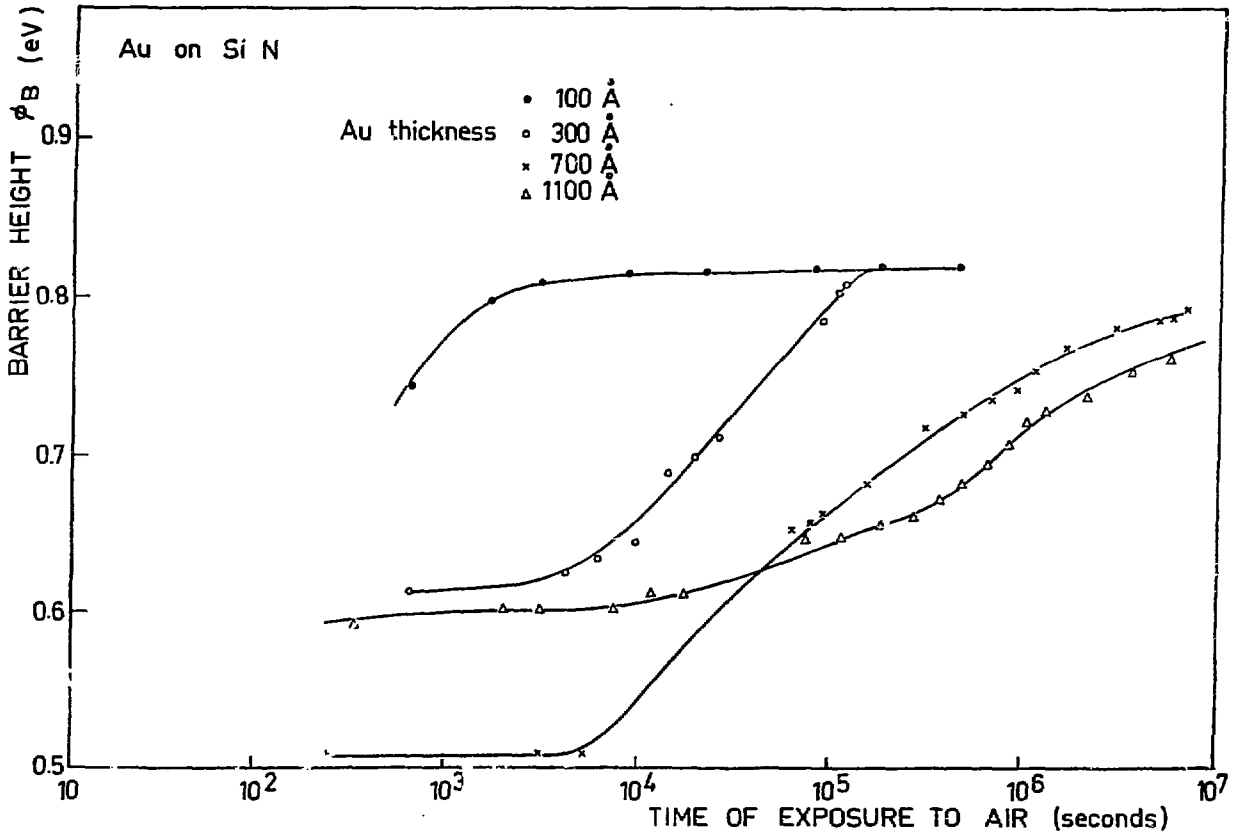
Au on Si N
Au thickness
• 100 Å
○ 300 Å
× 700 Å
△ 1100 Å
BARRIER HEIGHT ϕ_B (eV)
0.9
0.8
0.7
0.6
0.5
10
10^2
10^3
10^4
10^5
10^6
10^7
TIME OF EXPOSURE TO AIR (seconds)

Fig. 4

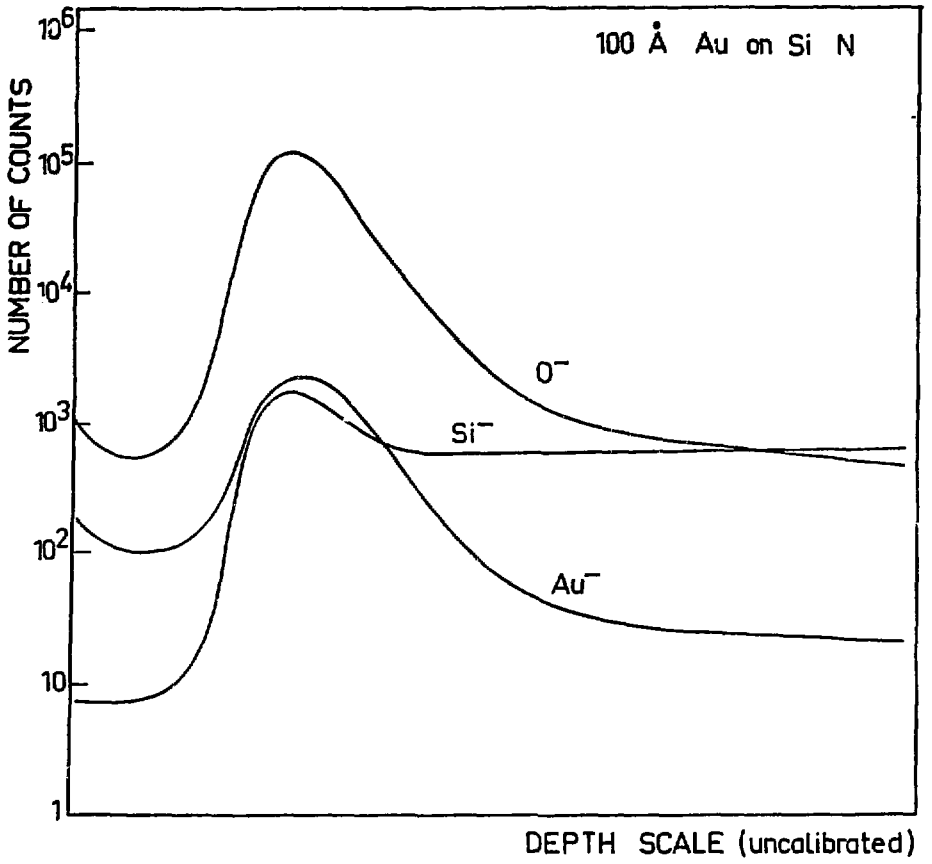
100 Å Au on Si N
NUMBER OF COUNTS
10^6
10^5
10^4
10^3
10^2
10
1
O^-
Si^-
Au^-
DEPTH SCALE (uncalibrated)

Fig. 5

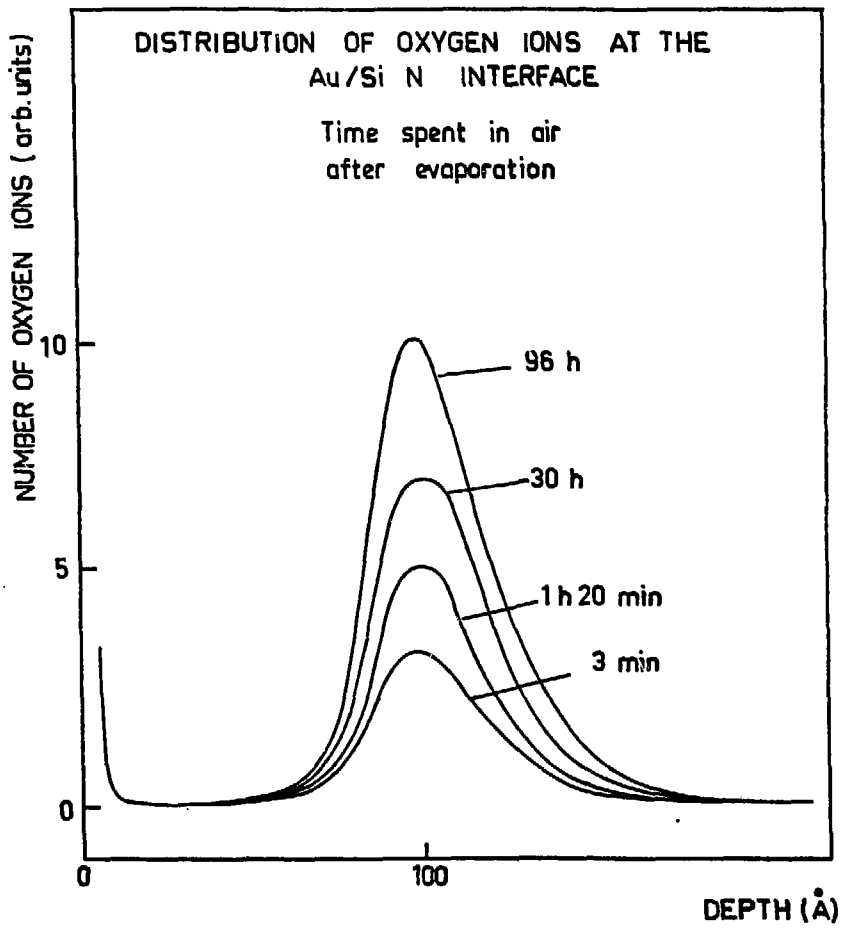
DISTRIBUTION OF OXYGEN IONS AT THE
Au/Si N INTERFACE
Time spent in air
after evaporation
NUMBER OF OXYGEN IONS (arb.units)
10
5
0
96 h
30 h
1 h 20 min
3 min
0
100
DEPTH (Å)

Fig. 6

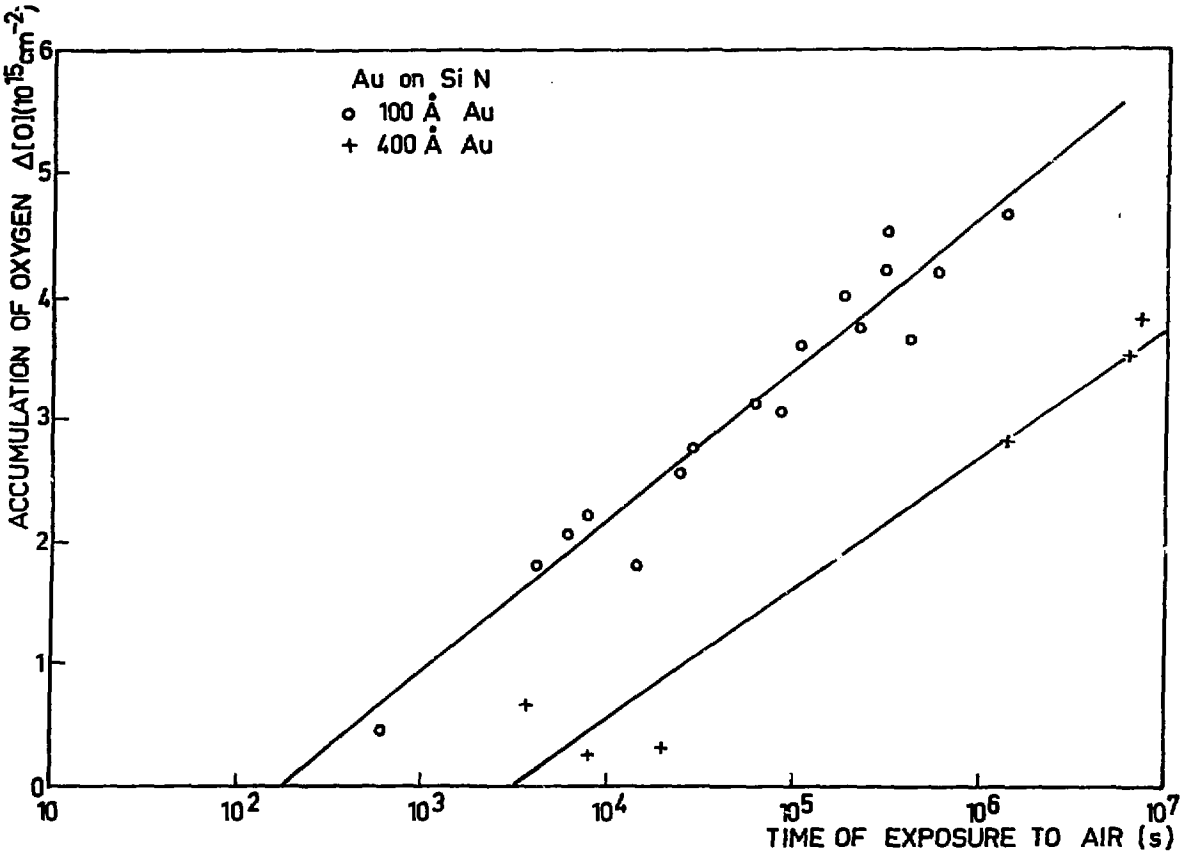
Au on Si N
o 100 Å Au
+ 400 Å Au
ACCUMULATION OF OXYGEN Δ[O](10^15 cm^-2)
TIME OF EXPOSURE TO AIR (s)
0
1
2
3
4
5
6
10
10^2
10^3
10^4
10^5
10^6
10^7

Fig. 7

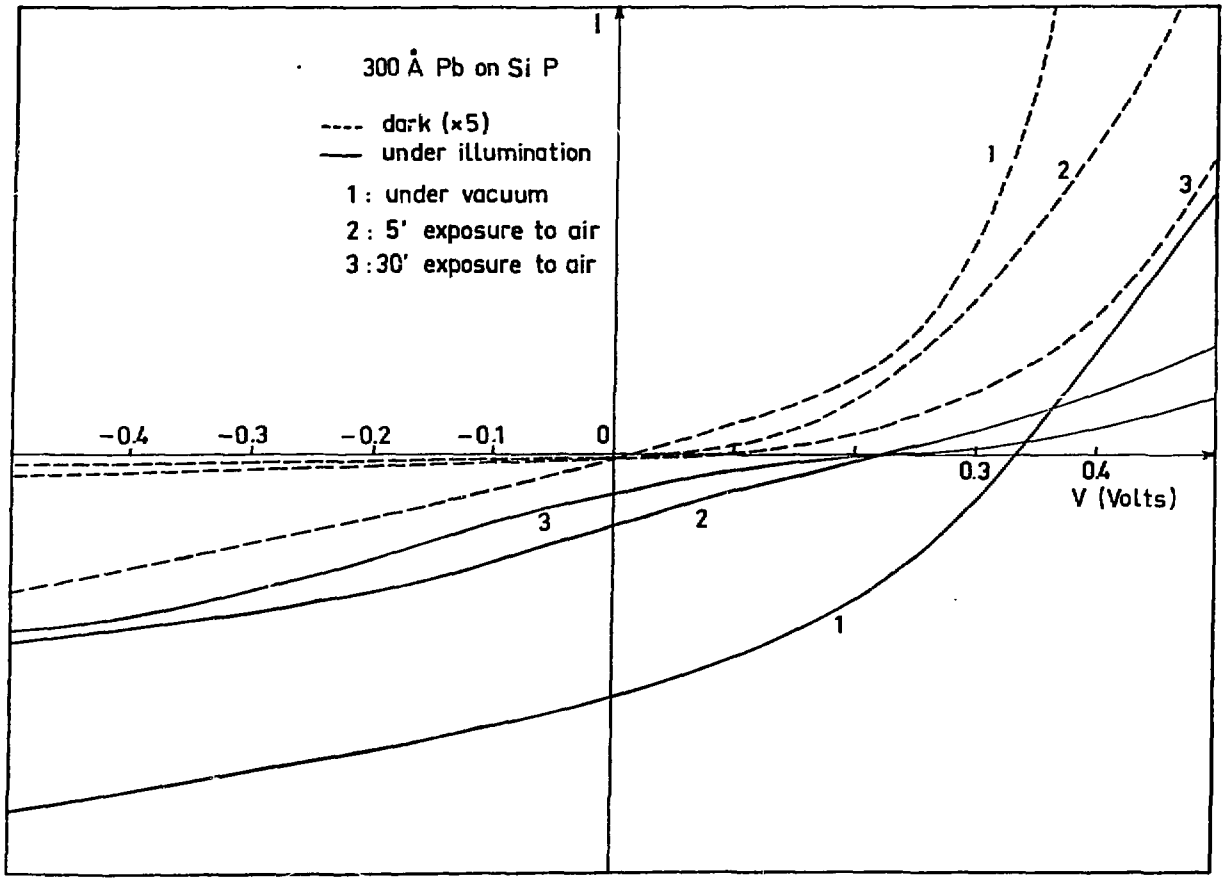
I
300 Å Pb on Si P
---- dark (×5)
—— under illumination
1 : under vacuum
2 : 5' exposure to air
3 : 30' exposure to air
−0.4
−0.3
−0.2
−0.1
0
0.3
0.4
V (Volts)
1
2
3
1
2
3

Fig. 8

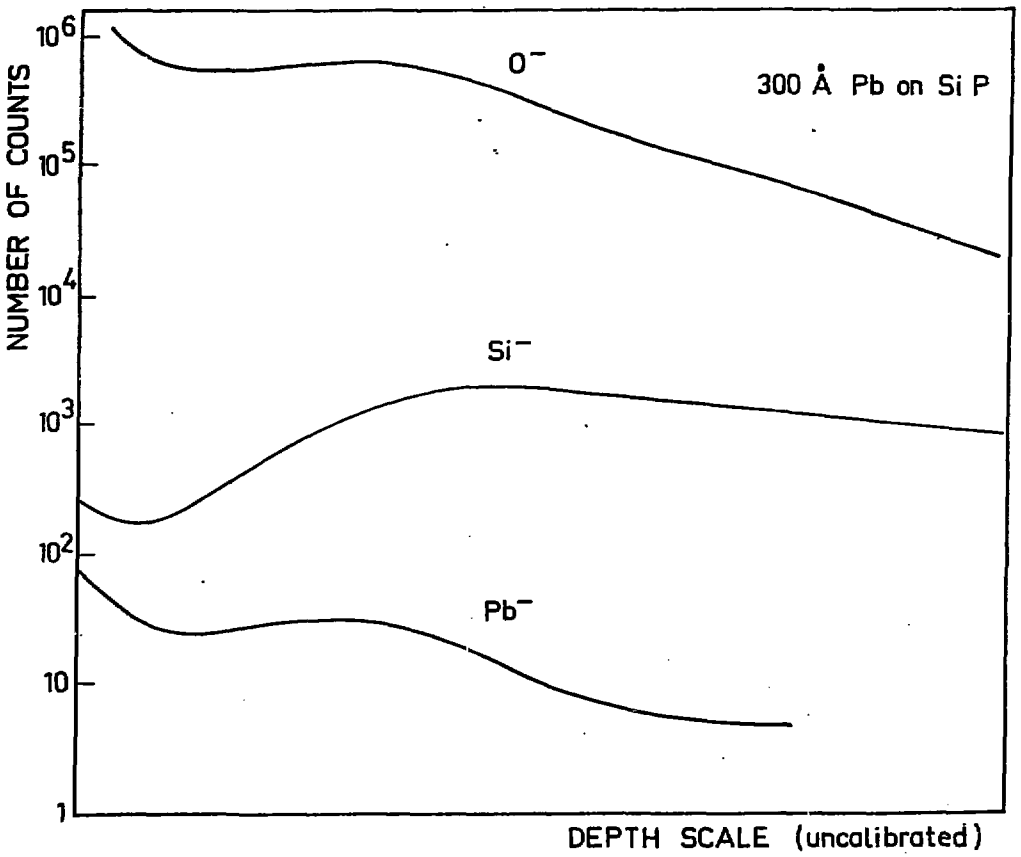
NUMBER OF COUNTS
10^6
10^5
10^4
10^3
10^2
10
1
O^-
300 Å Pb on Si P
Si^-
Pb^-
DEPTH SCALE (uncalibrated)

Fig. 9

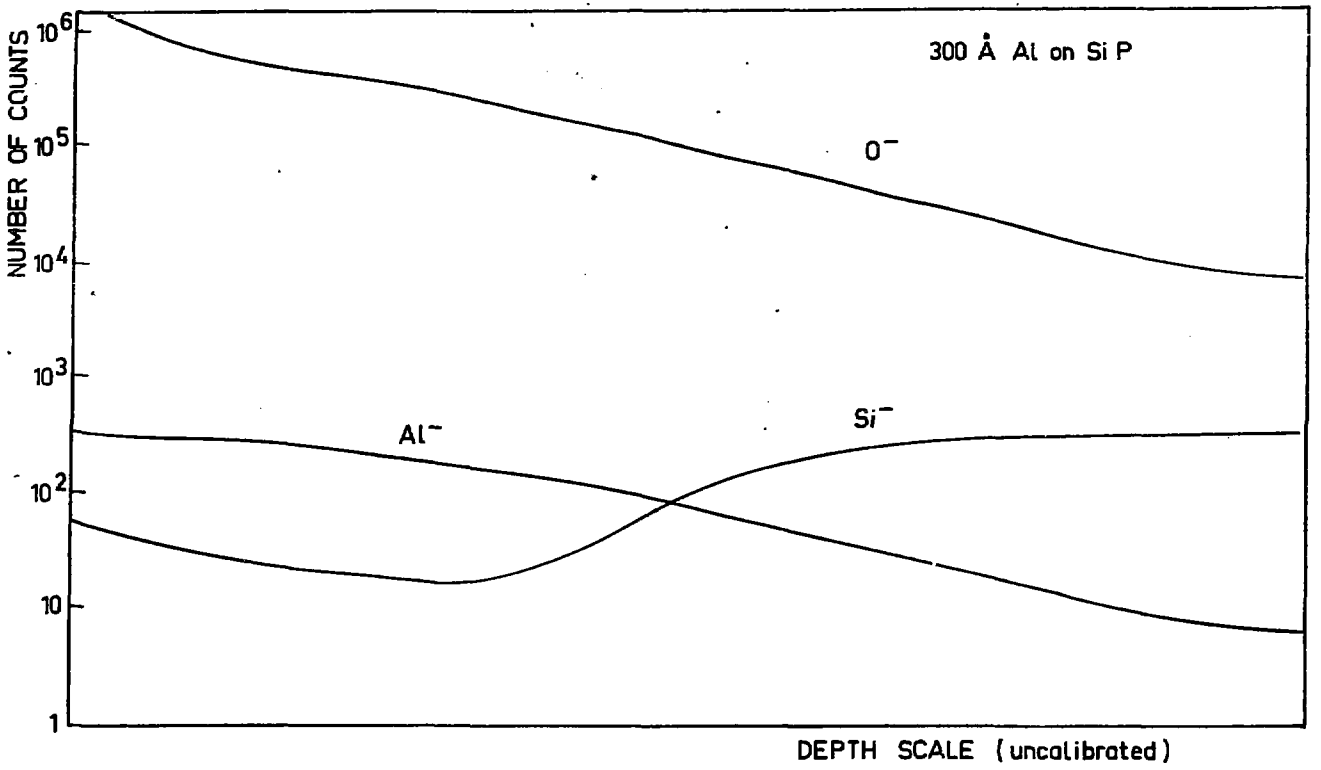
NUMBER OF COUNTS
10^6
10^5
10^4
10^3
10^2
10
1
300 Å Al on Si P
O^-
Al^-
Si^-
DEPTH SCALE (uncalibrated)

Fig. 10 a

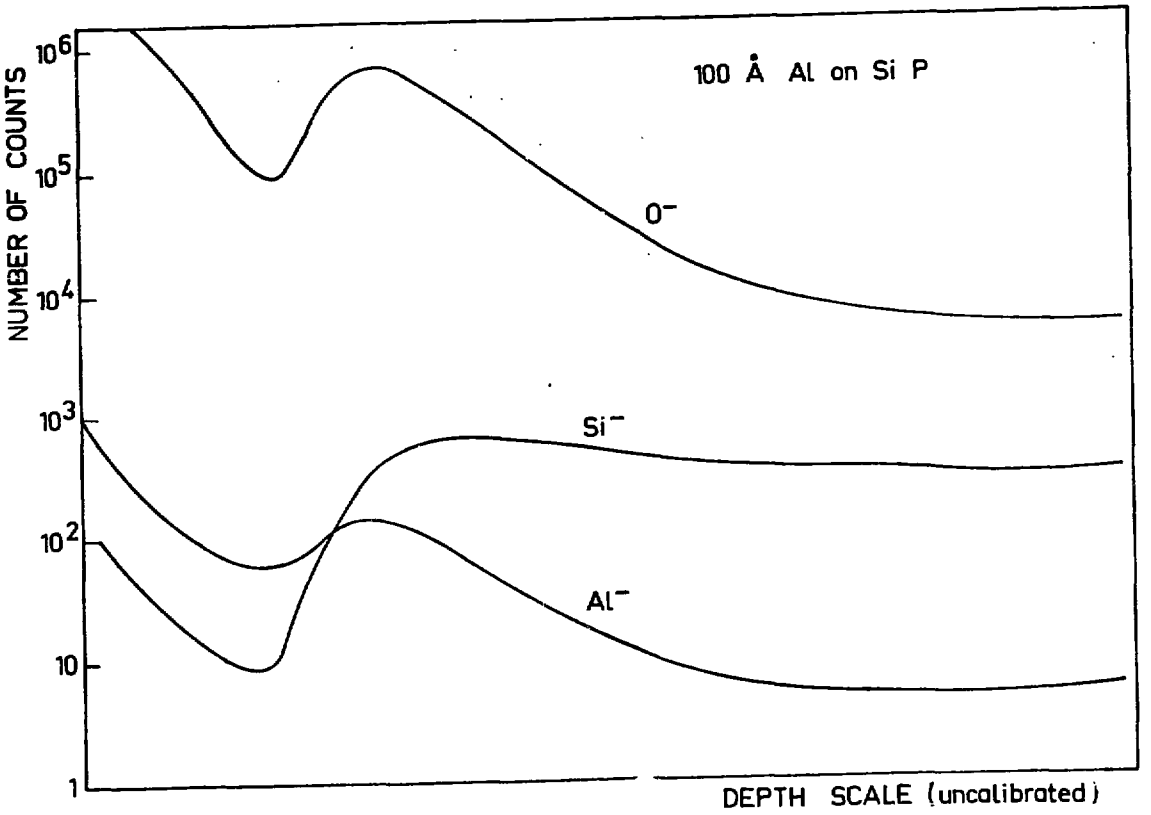
NUMBER OF COUNTS
10^6
10^5
10^4
10^3
10^2
10
1
100 Å Al on Si P
O^-
Si^-
Al^-
DEPTH SCALE (uncalibrated)

Fig. 10 b

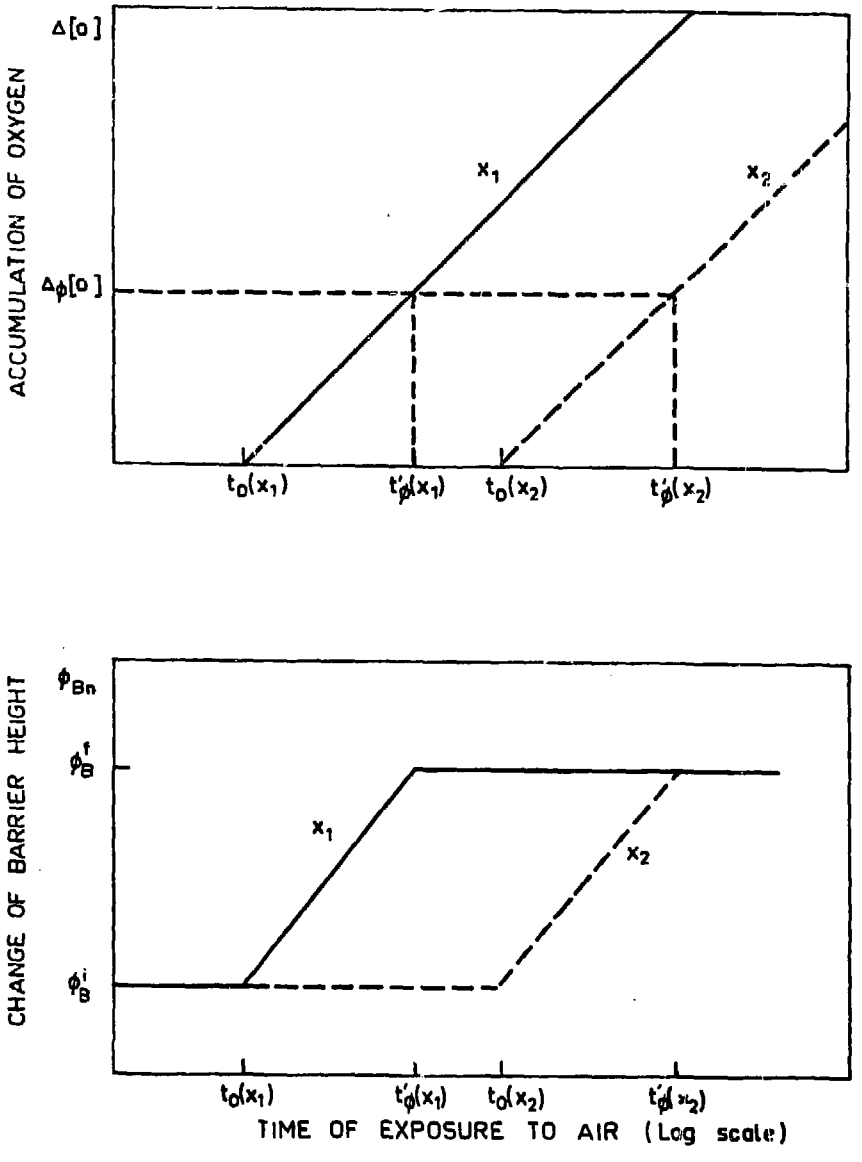
ACCUMULATION OF OXYGEN
Δ[o]
Δφ[o]
x1
x2
t0(x1)
t'φ(x1)
t0(x2)
t'φ(x2)
CHANGE OF BARRIER HEIGHT
φBn
φBf
φBi
x1
x2
t0(x1)
t'φ(x1)
t0(x2)
t'φ(x2)
TIME OF EXPOSURE TO AIR (Log scale)

Fig. 11