

N84 21987 ^{D7}

DIFFUSION BARRIERS

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The choice of the metallic film for the contact to a semiconductor device is usually predicated by considerations of economics, know-how, or precedence. The typical case is that the desired metal is unstable when forming a couple with the semiconductor. One way to try to stabilize a contact is by interposing a thin film of a material that has low diffusivity for the atoms in question. The solution is attractive because it is apparently simple and universal.

The difficulty is that the notion of a diffusion barrier is derived from bulk considerations. The time required to penetrate a layer by diffusion decreases with the square of the layer thickness. In addition, the relevant diffusivity in thin films is typically determined not by bulk diffusion, but by diffusion along extended defects, which can be many orders of magnitude faster than bulk diffusion at the temperatures encountered in device processing and operation. The defects in a film are strongly dependent on the method of deposition used and on the conditions prevailing during deposition. For diffusion barrier applications, the fabrication procedure is therefore as important as the choice of the material. This crucial point is often overlooked.

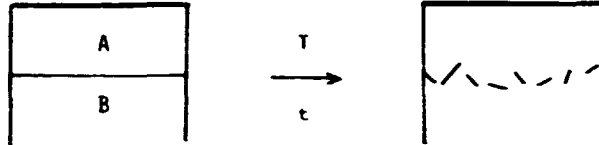
By their structure, thin-film diffusion barriers can be classified in single-crystalline, polycrystalline, and amorphous. Single-crystalline layers are unpractical, leaving only polycrystalline and amorphous layers as valid options. By their composition, thin-film diffusion barriers can be sub-divided into elemental and compound materials. For electrical contacts, only metallic media apply. Of these, most elemental metal films must be ruled out, because soluble metals dissolve, insoluble polycrystalline metals contain fast diffusion paths, and amorphous metals are not stable at room temperature. Metallic compound and alloys, polycrystalline or amorphous in structure, thus constitute the favored range of materials for electrically conducting thin-film diffusion barriers.

Three types of barriers can be distinguished. The stuffed barrier derives its low atomic diffusivity to impurities that concentrate along the extended defects of a polycrystalline layer. A number of very successful metallization systems are based on that concept. Sacrificial barriers exploit the fact that some (elemental) thin films react in a laterally uniform and reproducible fashion. When a thin film reacts in that fashion on both sides, and when these reactions proceed more rapidly than the diffusion through the film, an effective separation is accomplished as long as the film is not fully consumed in the reactions. Sacrificial barriers have the advantage that the point of their failure is predictable. Several successful sacrificial barriers are described in the literature, and a few new ones are under study at Caltech. Passive barriers are those most closely approximating an ideal barrier. The most-studied case is that of sputtered TiN films. The material has very low diffusivity for many metals, in spite of being fine-grained polycrystalline. The good kinetic properties of TiN are largely independent of the sputtering mode used for its deposition, which suggest that it is the very high melting point of TiN ($\sim 2400^\circ\text{C}$) that is the ultimate reason for its success, and not the presence of undetected impurities. TiN is an interstitial alloy, of which there is a fairly large number; a few others of these have also been shown to work well as thin-film diffusion barriers.

Stuffed barriers may be viewed as passive barriers whose low diffusivity material extends along the defects of the polycrystalline host. The same holds for barriers that form by a localized segregation of purposely introduced impurities (e.g. by ion implantation). New possibilities of diffusion barrier synthesis have been demonstrated with this approach. Amorphous metallic films offer another interesting way to obtain low diffusivity films. All amorphous diffusion barriers tested so far have been obtained by sputter-deposition. Both sacrificial and passive barriers can be conceived with amorphous films. Results obtained to date are quite encouraging, but the inclusion of an amorphous compound layer in a metallization system does not by itself suffice to ensure stability, as examples show.

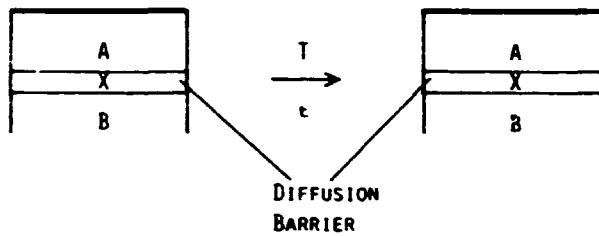
Problem and Solution

PROBLEM



METAL FILM ON SEMICONDUCTOR SUBSTRATE IS
RARELY STABLE - INTERDIFFUSION
- COMPOUND FORMATION

SOLUTION WITH DIFFUSION BARRIER



IDEAL BARRIER X

- LOW DIFFUSIVITY FOR A & B
- STABLE AGAINST A & B
- LATERALLY UNIFORM & HOMOGENEOUS
- ADHERES TO A & B
- RESISTS MECHANICAL, THERMAL STRESSES
- LOW CONTACT RESISTIVITY
- COMPATIBLE WITH DEVICE PROCESSING

COMPROMISING IS NECESSARY

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Difficulties

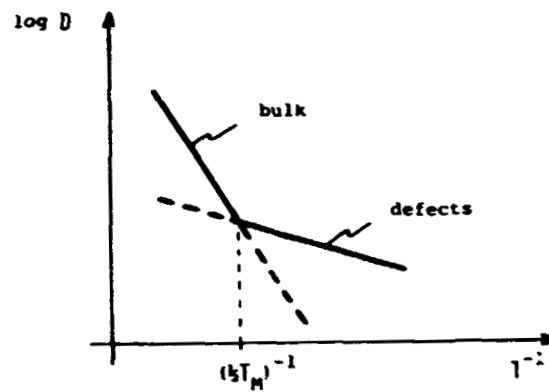
DIFFUSION ACROSS THIN FILMS IS FAST

$$x^2 \sim Dt \quad t \sim \frac{x^2}{D}$$

IF $t = 10$ YRS FOR 1 MM (10^{-1} CM)

FOR 1000 Å (10^{-5} CM) $t = 3$ SEC!

DEFECTS ENHANCE DIFFUSIVITIES IN THIN FILMS



$$D_{\text{FILM}} \gg D_{\text{BULK}} \text{ FOR } T < \frac{1}{2}T_M$$

Defects in Thin Films

FUNCTION OF - DEPOSITION METHOD
- DEPOSITION PARAMETERS

DIFFUSIVITIES = f (METHOD, PARAMETERS)

TWO PERTINENT QUESTIONS FOR DIFFUSION BARRIERS:

1. WHAT MATERIAL?
2. PREPARED HOW?

ADDRESSING QUESTION 1 IS NOT SUFFICIENT.

Thin-Film Diffusion Barriers

STRUCTURE

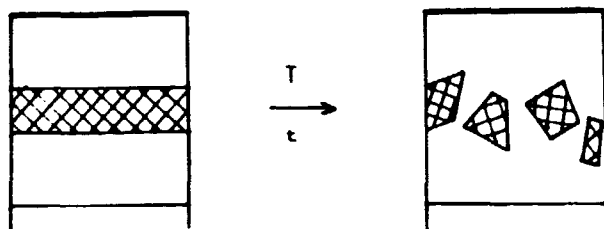
SINGLE-CRYSTAL	
Minimal Defects	unpractical
Minimal Diffusivities	
AMORPHOUS	
No Extended Defects	attractive
Low Diffusivities	novel
POLYCRYSTALLINE	
Extended Defects	practical
High Diffusivity Paths	problematic

PRACTICAL BARRIERS

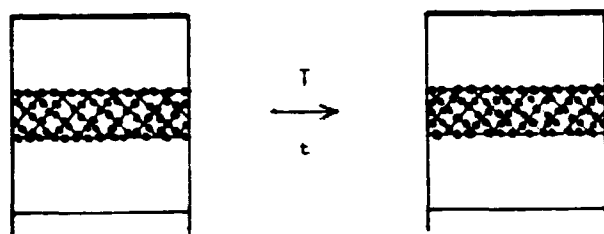
ELEMENTAL, POLYCRYSTALLINE	
Miscible with A and B	fail
Immiscible with A and B	fail
COMPOUNDS, POLYCRYSTALLINE	
Stuffed Barrier	hold
Sacrificial Barrier	hold
Passive Barrier	hold
COMPOUNDS, AMORPHOUS	hold

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Stuffed Barrier



PURE BARRIER FAILS



IMPURE (STUFFED) BARRIER HOLDS

EXAMPLES

<Si>/Ti-W/Au/

<Si>/Cr+Cr OXIDES/Al/

<Si>/Al+Al₂O₃/Al/

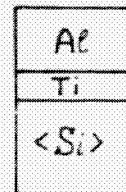
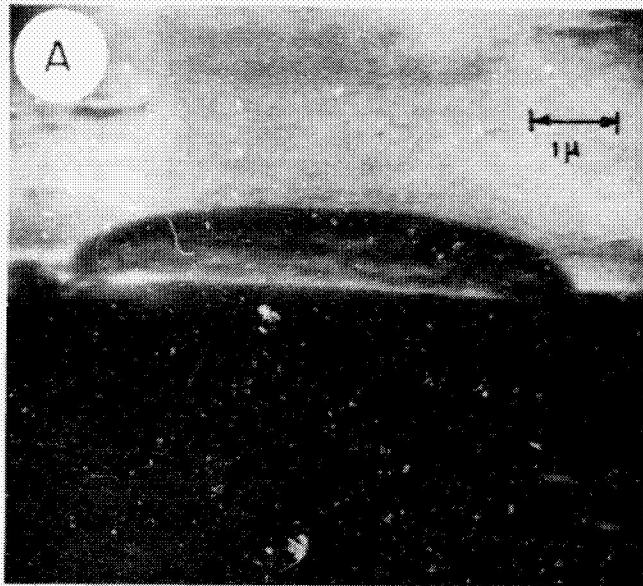
<Si>/Ta+Ta₂O₃/Al/

J.E. BAKER ET AL., THIN SOLID FILMS, 69 (1980) 5

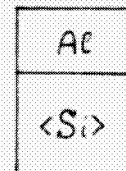
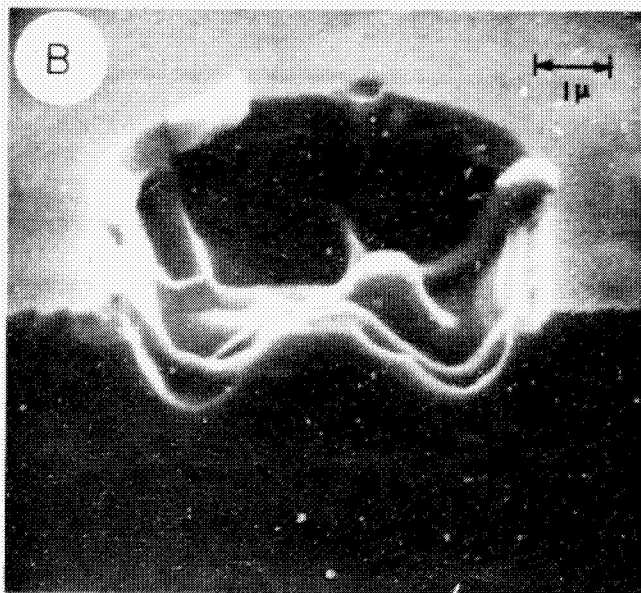
H.M. DALAL ET AL., U.S. PATENT 4,214,256 (JULY '8

W.K. CHU ET AL., U.S. PATENT 4,206,472 (JUNE 198

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*Sacrificial
Ti Barrier*



U.S. Patent Jul. 22, 1980 Sheet 1 of 4 4,214,256

H. M. DALAL, M. GHAFGHAI, L. A. KASPRZAK, AND H. WIMPFHEIMER,
IBM

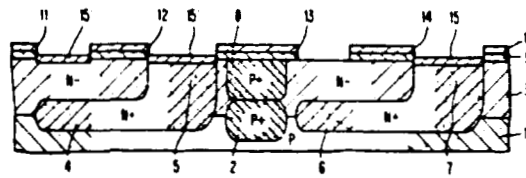
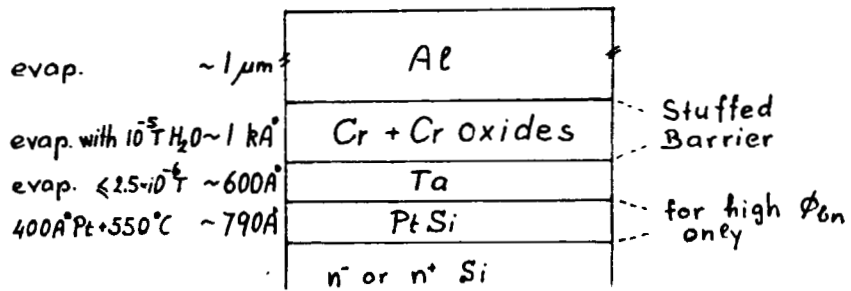


FIG. 1C



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U.S. Patent Jun. 3, 1980 Sheet 1 of 2 4,206,472

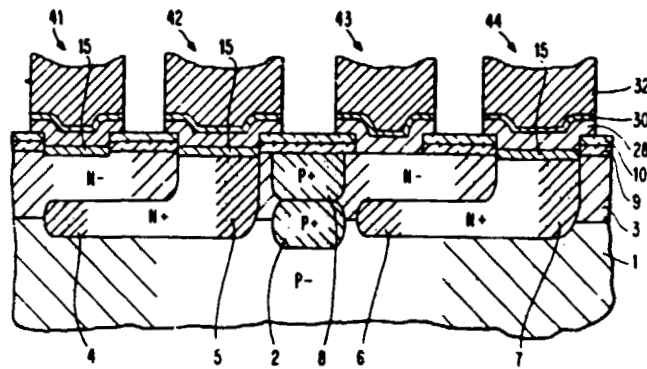
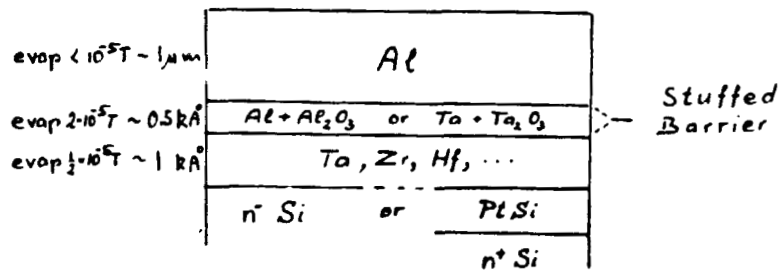
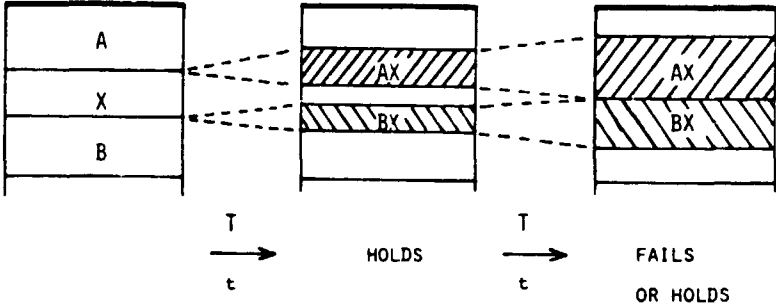


FIG. 1



Sacrificial Barrier



CONDITIONS ON REACTION OF X WITH A AND B:

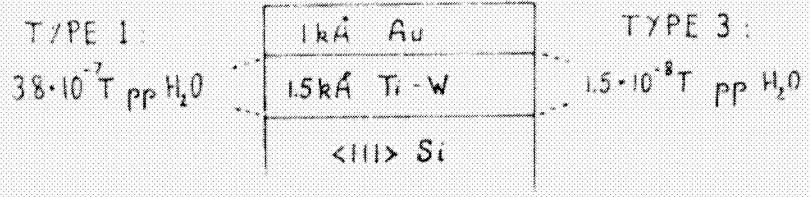
- Laterally uniform
- Reproducible and characterized
- Faster than diffusion through A, X, B

EXAMPLES*

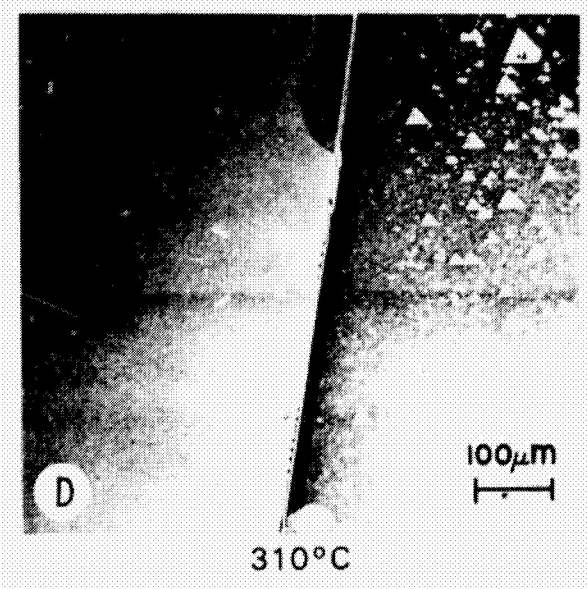
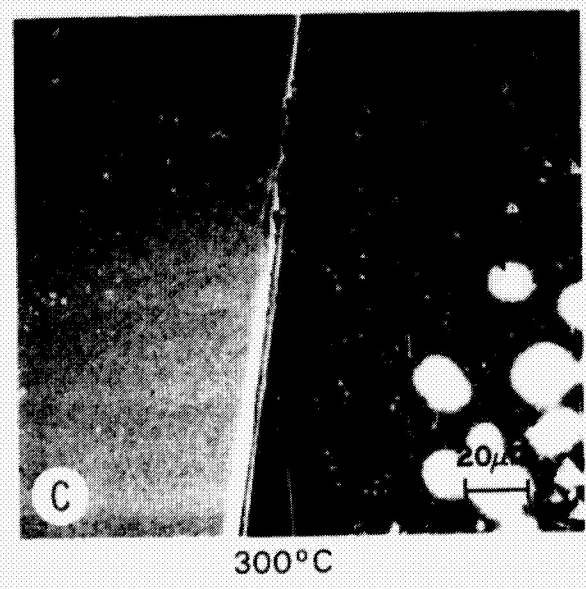
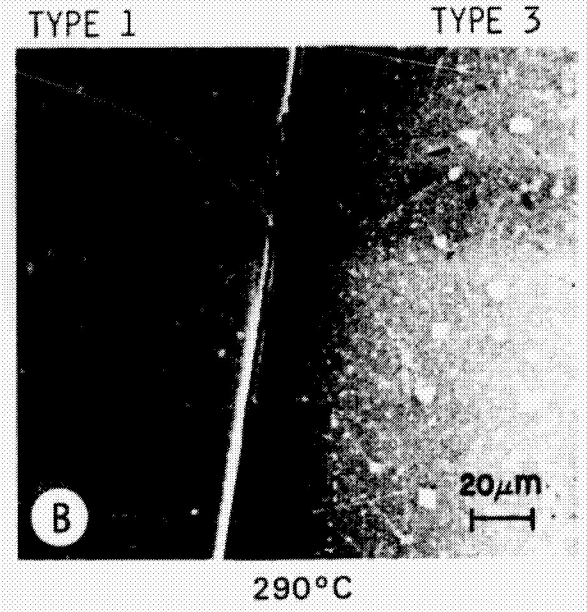
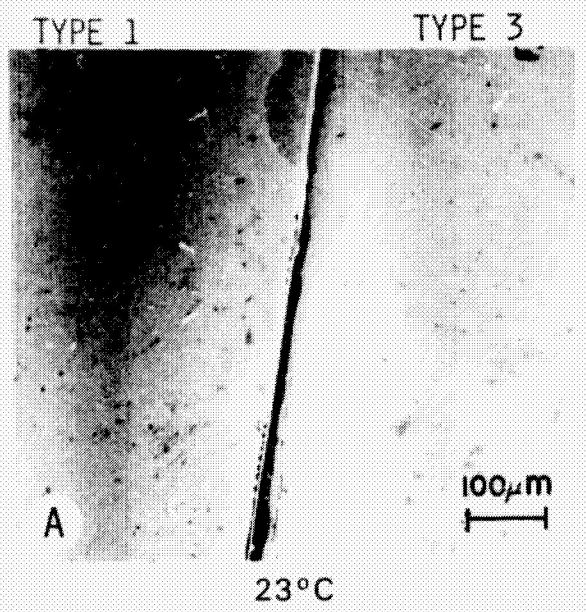
<Si>/Ti/Al/	R.W.BOWER, APPL. PHYS. LETT., <u>23</u> (1973)99.
<Si>/Ta/TaAl ₃ /Al/	J.K.HOWARD ET AL., U.S. PATENT 4,201,999 (MAY 1980).
<Si>/Pd ₂ Si/Ti/Al/	G.SALOMONSON ET AL., PHYSICA SCRIPTA, <u>24</u> (1981)401.
<Si>/PtSi/Ti/Al/	
<Si>/NiSi/Cr/Al/	M.BARTUR, (TO BE PUBLISHED).
<Si>/PtSi/Cr/Al/	

REMARKS: *STUDIES TESTING BOTH METALLURGICAL AND ELECTRICAL STABILITY.

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23°C - 400°C, 6°C/MIN



REF.: J. E. BAKER, R. J. BLATTNER, S. NADEL, C. A. EVANS, JR. AND
R. S. NOWICKI, THIN SOLID FILMS, 69, 53 (1980).

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U.S. Patent May. 6, 1960 4,201,999

J. K. HOWARD, F. E. TURENE, AND J. F. WHITE, I.B.M.

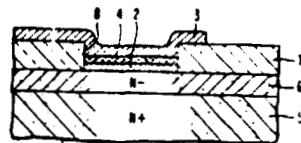
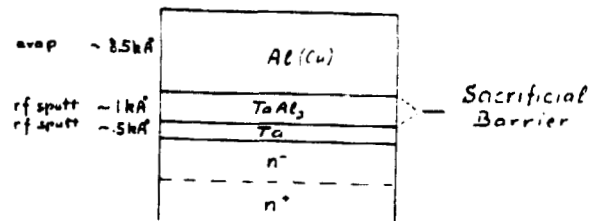
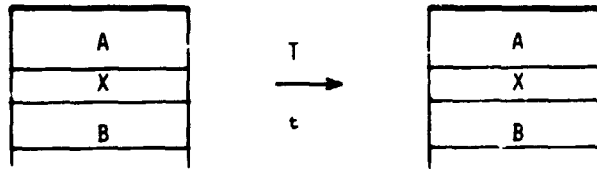


FIG. 1



Passive Barrier



EXAMPLES*

STUFFED BARRIERS

INTERSTITIAL COMPOUNDS

Ti/TiN/Pt/

<Si>/TiN/Ti/Ag/

<Si>/NiSi/TiN/Al/
<Si>/Pd₂Si/TiN/Al/

<GaAs>/Ge-Au-Pt/TiN/Ti-Pt-Au/ R.D.REMBA ET AL. (UNPUBLISHED).

IMPLANTED IMPURITY

<Si>/Ni:O/

<Si>/Ni:N/

AN ALTERNATE VIEW OF THEM

C.W.NELSON (1969)

P.R.FOURNIER, U.S.PATENT 3,879,746(1975).

W.J.GARCEAU & G.K.HERB, THIN SOLID FILMS,
53(1978)193.

N.CHEUNG ET AL., J.APPL.PHYS. 52(1981)4297.

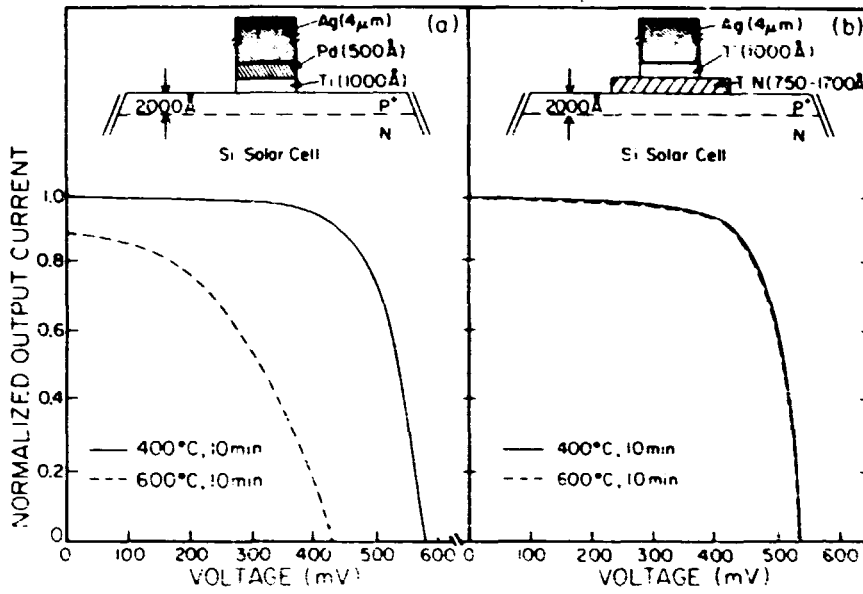
M.FINETTI ET AL. (TO BE PUBLISHED).

D.S.SCOTT, J.VAC.SCI.TECHNOL. 19(1981)786.

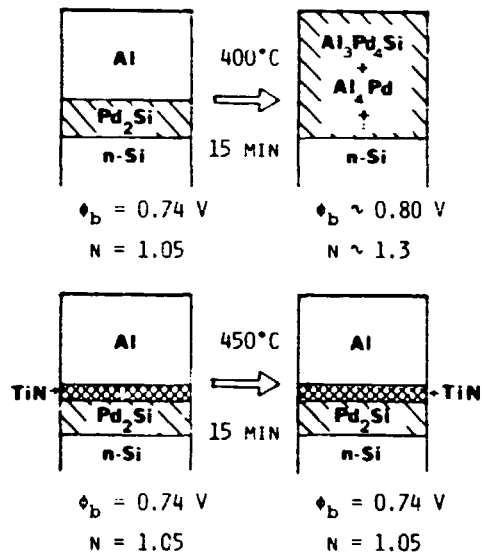
T.BANWELL ET AL. (TO BE PUBLISHED).

REMARKS: *STUDIES TESTING BOTH METALLURGICAL AND ELECTRICAL STABILITY

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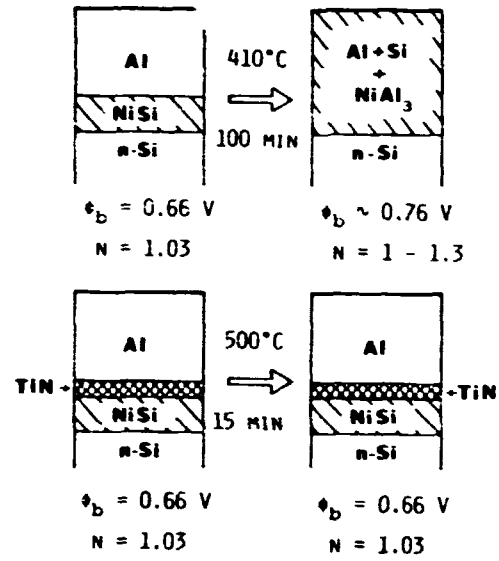


Al-Pd₂Si-n-Si Schottky Diode

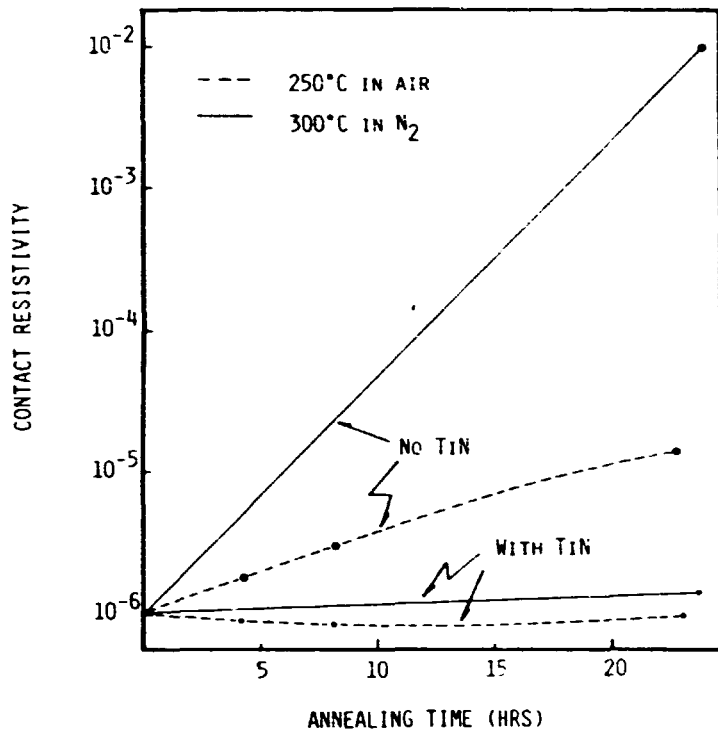
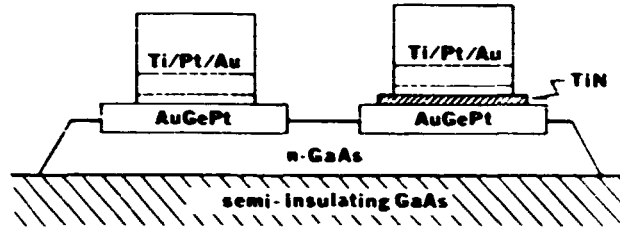


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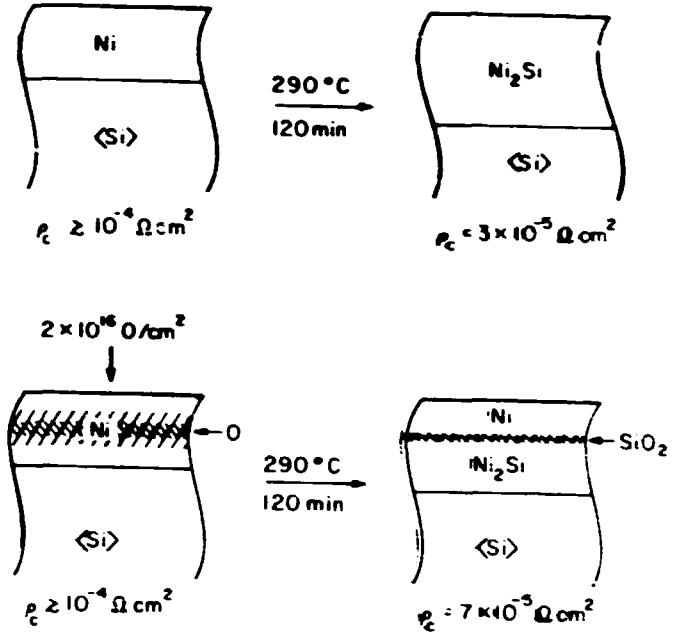
Al-NiSi-n-Si Schottky Diode



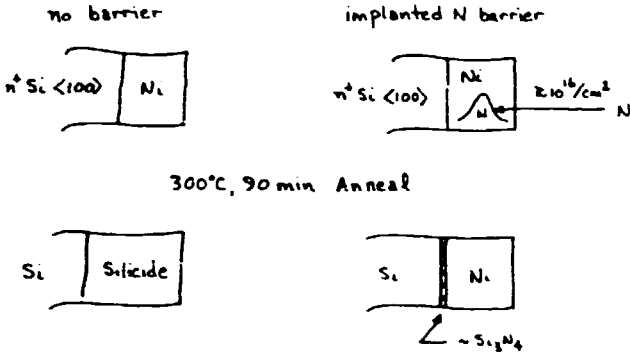
Ohmic Contacts to GaAs



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Implanted N Diffusion Barrier



300°C, 90 min Anneal

Sequential Annealing
@ 50°C increments

phase(s)	ρ_c $\Omega \cdot \text{cm}^2$		phase(s)	ρ_c $\Omega \cdot \text{cm}^2$
NiSi/Ni ₂ Si	1.0×10^{-4}	300°C 90 min	Ni	6.3×10^{-5}
NiSi	1.0×10^{-4}	350°C 30 min	Ni	7.1×10^{-5}
NiSi	1.1×10^{-4}	450°C 30 min	Ni	6.7×10^{-5}
NiSi	1.0×10^{-4}	550°C 30 min	Ni	7.7×10^{-5}
NiSi	1.3×10^{-4}	650°C 30 min	non uniform NiSi	5.6×10^{-5}

ABBREVIATED TABLE OF RESULTS

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Amorphous Barrier

rf SPUTTERED FE-W

2kÅ	Ag
1kÅ	Fe ₄₅ W ₅₅
	Si
	N ⁺ & P ⁺

	$\rho_c (10^{-6} \Omega\text{cm}^2)$	
	AS-DEPOSIT.	500°C 30 MIN.
N ⁺ Si	0.10	0.10
P ⁺ Si	2.8	1.1

N Si $\rho_c \sim 71 \Omega\text{cm}^2$, $\phi_{BN} = 0.61 \text{ eV}$

M. FINETTI ET AL., APPL. PHYS. LETT. (IN PRESS).

rf SPUTTERED MULTILAYERS AND 500°C, 4 H ANNEALING

~1.3kÅ	Au	NO DEGRADATION OF I(V) AFTER 400°C, 16 H	Au	*SIMILAR RESULT 450°C, 8 H
	W-Si		W-Si OR Ti-W-Si	
	N<GAAS>		<INP>	

GAAs MESFET

WITH TiW-Si BARRIER: STABLE AT 300°C PAST 944 H (39 D)

WITHOUT TiW-Si BARRIER: FAILS AT 300°C AFTER 360 H (15 D)

W. T. ANDERSON ET AL. THIN SOLID FILMS (IN PRESS).

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Amorphous Barrier: Metallurgical Studies

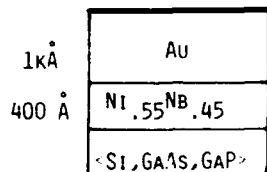
SPUTTERED AMORPHOUS BARRIERS	T_c (1 H)
<SI>/NI-NB/AU OR CU/ <GAAS>/NI-NB/CU/ <GAP>/NI-NB/AU/	$Ni_{.57}Nb_{.43} \cong 575^\circ C$
<SI>/MO-SI/AU OR CU/ <GAAS>/MO-SI/CU/ <GAP>/MO-SI/AU/	$Mo_{.60}Si_{.40} \cong 550^\circ C$
<SI>/W-SI/AU OR CU/	$W_{.85}Si_{.15} \cong 700^\circ C$

FAILS AT $T \cong T_c$ FOR SI

$T < T_c$ FOR GAAS, GAP

K.J.GUO ET AL., IEEE - 81CH1658-4, P.35 (1981).

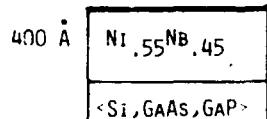
J.D.WILEY ET AL., IEEE TRANS. IE-29, NO.2, 154 (1982).



$T_c \cong 600^\circ C$ (1 H)

FAILS AT $600^\circ C$, 15 MIN.

DE AT $600^\circ C$, 15 MIN. $\cong 500 \text{ \AA}$



FAILS AT $T \cong T_c$ FOR SI, GAP

$< T_c$ FOR GAAS

B.L.DOYLE ET AL., THIN SOLID FILMS (IN PRESS).

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Summary

THIN FILMS ≠ BULK

DEFECTS CONTROL KINETICS

DEFECTS = $f(\text{FAB. PROCESS})$

DIFFUSION BARRIERS = $f(\text{FAB. PROCESS})$

MISCIBLE ELEMENTAL BARRIERS FAIL

IMMISCIBLE ELEMENTAL BARRIERS FAIL

STUFFED BARRIERS

HOLD

Ti/Mo/Au

Si/Ti+W/Au

Ta/CR/AL

Ta/AL/AL

⋮

⋮

SACRIFICIAL BARRIERS

HOLD

Si/Ti/AL

Pd₂Si/CR/AL

⋮

⋮

PASSIVE BARRIERS

HOLD

TIN

IMPLANTED IMPURITIES

AMORPHOUS

THERE IS HOPE

DISCUSSION

CAMPBELL: Titanium nitride is a passive barrier. Is that the compound titanium nitride?

NICOLET: Yes. It is a compound. It is TiN.

CAMPBELL: Stoichiometric.

NICOLET: In our case it is very close to stoichiometric. It is easy by reactive sputtering. It is easy to produce reactively in stoichiometric form. It is just as easy to produce it reactively in nonstoichiometric form, it is just as easy to produce as in dirt form. As a matter of fact, an interesting idea is why would you not intentionally have a little dirt in Ti-nitride. It might actually make it even better. That is one thing we wanted to try. It looks like heresy. But it is also heresy to apply oxygen to nickel if you talk to the silicon community. I think that there is lots of room to try new ideas in this business. Yes, it is just simple Ti-nitride, however, Ti-nitride isn't simple.

SOMBERG: You mentioned in the beginning that the pure-metal systems like Ti-palladium-silver doesn't work. Could it be that they really are not pure-metal systems, that they are "dirty" systems, that there are other things going on?

NICOLET: Well, that is possible. The Motorola system of electroplated nickel copper, for example, surely has a lot of phosphorus in it and you can make nickel amorphous if you have enough phosphorus in it. It doesn't have to be but it could be. We have looked at this and it is possible. What I was trying to say is if you make things pure the way you write it down, when you say it's nickel, you mean it's nickel not nickel plus a lot of other things. Many things fail. And it is important to make that distinction. Otherwise you will get lost. It becomes black magic and people will not tell you what they do. This is just a sign that it is not understood.

AMICK: Would you comment, please, on the adhesion properties when you implant either oxygen or nitrogen into the nickel and then form this interfacial layer, which is apparently either a nitride or an oxide. What happens to the adhesion properties of that system?

NICOLET: We haven't looked at that much. I will tell you my reluctance to get into this type of question. It is something that I would like very much to consider in our measurements, but I can't conceive of our Caltech graduate students making adhesion measurements.

COMMENT: It is not that expensive.

NICOLET: It's not expensive, but if you can't write down the Schroedinger equations, that is a complaint. If I have someone in industry or elsewhere who would like to collaborate, it would be delightful, but we don't cover that part well, and I don't know how to do it. I know that

I will not get anywhere with this proposition with anybody in my group. I think the way to do that is by collaboration. I think it would be very nice to investigate. The same question for Ti-nitride. Ti-nitride has to be fixed in one fashion or another to have proper adhesion. And that should also be fixed. But I think these things can be resolved.

WONG: Did you, or did anyone else, have any diffusion failure of amorphous alloy?

NICOLET: Yes. Data on diffusion in amorphous alloys are plentiful in bulk. Data on amorphous materials is 20 years old now. A thick compendium. What you really want are the data on diffusion in thin films, that are amorphous. Maybe that is different. There are a number of measurements that were done and they are much more limited. Typically, what people do, they make an amorphous layer and they implant heavy material, like gold. With backscattering you can see how the diffusion takes place. And you see dramatic differences if you compare the same layer amorphized or crystallized. If you have a crystallized layer and implant an amorphous layer and you do the annealing at the same low temperatures the diffusivity is vastly different. That's only half the story, and as we found out with our aluminum layer, you might have very low diffusivity inside but if you have sufficiently thick layers with large diffusivity on the top you might just lose your layer in a hurry. You may not crystallize. It might just be dissolved.

WONG: In this sense, in that example that you showed in the viewgraph, can we do something to saturate the aluminum with whatever -- the iron tungsten, for example -- so that we don't have diffusion during that period?

NICOLET: That would be another idea. Yes, that would be good to try that. Let me just first explain. While we were making these measurements, how frustrating we found it when we failed. But I thought, no, we haven't failed, because it opened our eyes to a lot of problems that are very relevant because you have to recognize this: you have bulk diffusivity in all directions.