N85-32427

AMORPHOUS METALLIC FILMS IN SILICON METALLIZATION SYSTEMS

CALIFORNIA INSTITUTE OF TECHNOLOGY

Marc-A. Nicolet
Hannu Kattelus
Frank So

The general objective of this project is to determine the potential of amorphous metallic thin films as a means of improving the stability of metallic contacts to a silicon substrate. The specific objective pursued in the reporting period was to determine the role of nitrogen in the formation and the resulting properties of amorphous thin-film diffusion barriers.

Amorphous metallic films are attractive as diffusion barriers because of the low atomic diffusivity in these materials. Our previous investigations have revealed that in meeting this condition alone, good diffusion barriers are not necessarily obtained, because amorphous films can react with an adjacent medium (e.g., Si, Al) before they recrystallize. In the case of a silicon single-crystalline substrate, correlation exists between the temperature at which an amorphous metallic binary thin film reacts and the temperatures at which the films made of the same two metallic elements react individually. We thus investigated amorphous binary films made of Zr and W, both of which react with Si individually only at elevated temperatures. We confirmed that such films react with Si only above 700°C when annealed in vacuum for 30 min.

When these films are in contact with metallic polycrystalline films (Ag, Al, Au, Ni); however, they react at significantly lower temperatures. The question arises how the reactivity of an amorphous metallic thin-film diffusion barrier can simultaneously be reduced on both sides of the film (substrate and metallization). Conceptual solutions do exist if the reactivity of two amorphous binary metallic thin films is low.

Amorphous W-N films were also investigated. They are more stable as barriers between Al and Si than polycrystalline W. Nitrogen effectively prevents the W-Al reaction that sets in at 500°C with polycrystalline W. In this respect, amorphous W-N films even outperform TiN diffusion barriers.

The study of W-N will continue, and that of Zr-N is planned, to determine deposition conditions that yield amorphous layers and how the properties vary with deposition conditions, using backscattering spectrometry, X-ray diffraction, and sheet resistivity measurements and transmission electron microscopy (TEM) for analysis.

Previous Findings

Amorphous Films (Mo-Ni, Ni W):

- React with Si substrate and Al overlayer below crystallization temperature T_c (600, 650°C).
- Ni diffuses into Si substrate. W diffuses into Al overlayer.
- Ni-Si reaction interfacially controlled and laterally confined.
- Adding N (Ni-N-W) lowers T_c to $\simeq$ 600°C, suppresses Ni-Si reaction below 725°C and Al-W reaction up to 550°C.

Approaches

Ways to circumvent reaction:

- Avoid Ni (and Co, Pd, Pt), e.g. Zr-W.
- Ternary amorphous films, e.g. Ni-N-W.
- Use buffer layer, e.g.

(A) Ni-W
NiSi
<Si>

- Multilayered amorphous films.

Results on Amorphous $W_{60}Zr_{40}$ Films

EXPERIMENTAL PROCEDURES:

- ON <100> N-TYPE SI AND SiO_2 SUBSTRATES.
- R.F. SPUTTERING, 10 MTORR AR, 300 W, 5",
  60 Å/MIN; (2 x 10^{-6} TORR VACUUM).
- EVAPORATED METAL FILMS (AL, AU, AG, NI)
  (3 x 10^{-7} TORR).
- ANNEALING IN VACUUM $\leq$ 5 x 10^{-7} TORR,
  30 MIN.
- RBS AND X-RAY DIFFRACTION.

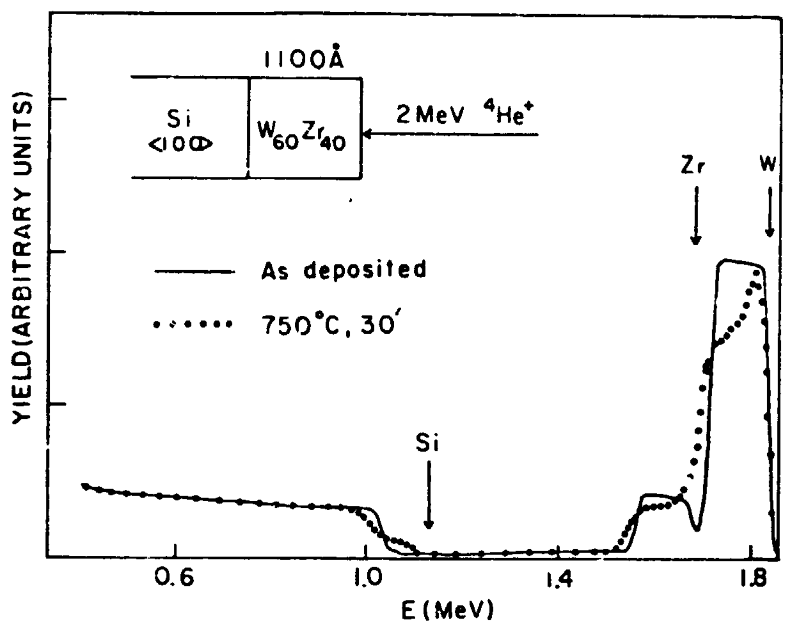
Crystallization on SiO_2

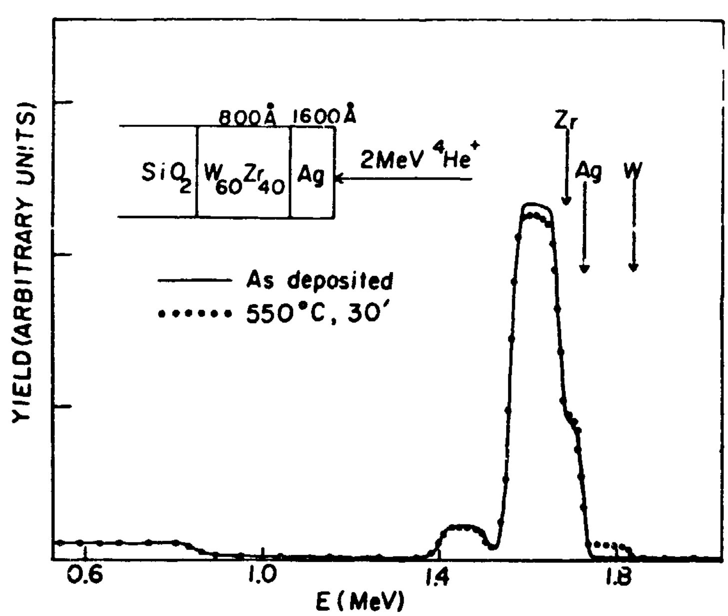
INTERACTION WITH <SI> SUBSTRATE.

- STABLE BELOW 700°C.
- UNIFORM REACTION AT 750°C
  ($\rightarrow WSi_2$, ZRSI OR Zr_2Si) SEE FIG. 1
- SAME AS W, ZR FILMS ON <SI>.
- SI IS DIFFUSING SPECIES, NOT W, ZR
  (NO INTERFACIAL PENETRATION OF <SI>)
  REACTION AT $T < T_c$.

<u>CONCLUSION</u>

AVOIDING NI (CO, PD, PT) IS BENEFICIAL.


1100Å
Si
<100>
$W_{60}Zr_{40}$
2 MeV $^4He^+$
Zr
W
As deposited
750°C, 30′
Si
YIELD (ARBITRARY UNITS)
0.6
1.0
1.4
1.8
E (MeV)


800Å
1600Å
SiO_2
$W_{60}Zr_{40}$
Ag
2MeV $^4He^+$
Zr
Ag
W
As deposited
550°C, 30′
YIELD (ARBITRARY UNITS)
0.6
1.0
1.4
1.8
E (MeV)

Interaction With Au, Ag, Al and Ni Overlayers: Reactions Below T_C

METAL	AU	AG	AL	NI
FILM THICKNESS (Å)	∿ 500	∿ 1600	1200	1300
REACTION TEMPERATURE (°C)	∿ 400	∿ 550	∿ 550	∿ 550
COMPOUND PHASES AT 550°C	AuW $AuZr_2$ $AuZr_3$	AgZr	Al_3Zr $Al_{12}W$	NiZr

- REACTION LATERALLY UNIFORM FOR NI ONLY.
- PENETRATION OF W INTO AG GRAIN BOUNDARIES SEE FIG. 2.

Schematic of $W_{60}Zr_{40}$-Ag Reaction

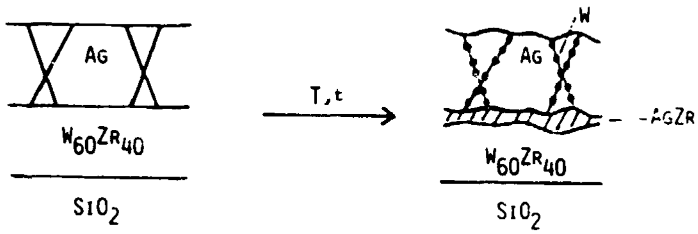
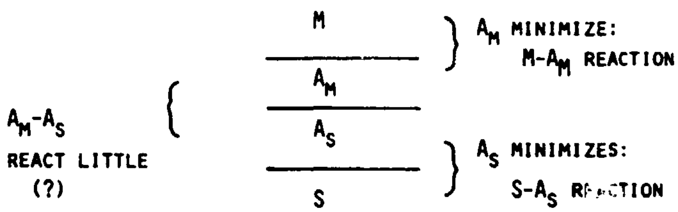


FIG. 3

CONCLUSIONS

AMORPHOUS W-ZR FILMS NOT OPTIMIZED FOR STABILITY WITH METAL OVERLAYER.

- CONCEPTUAL REMEDY: AMORPHOUS BILAYER



CONCENTRAT' ON MINIMIZING M-A_M REACTIONS.

Results on Amorphous W-N Films

- Ni-N-W superior to Ni-W with Al.
- Investigate W-N versus W
  W-N versus ZrN
  W-Zr-N.

Experimental Procedures:

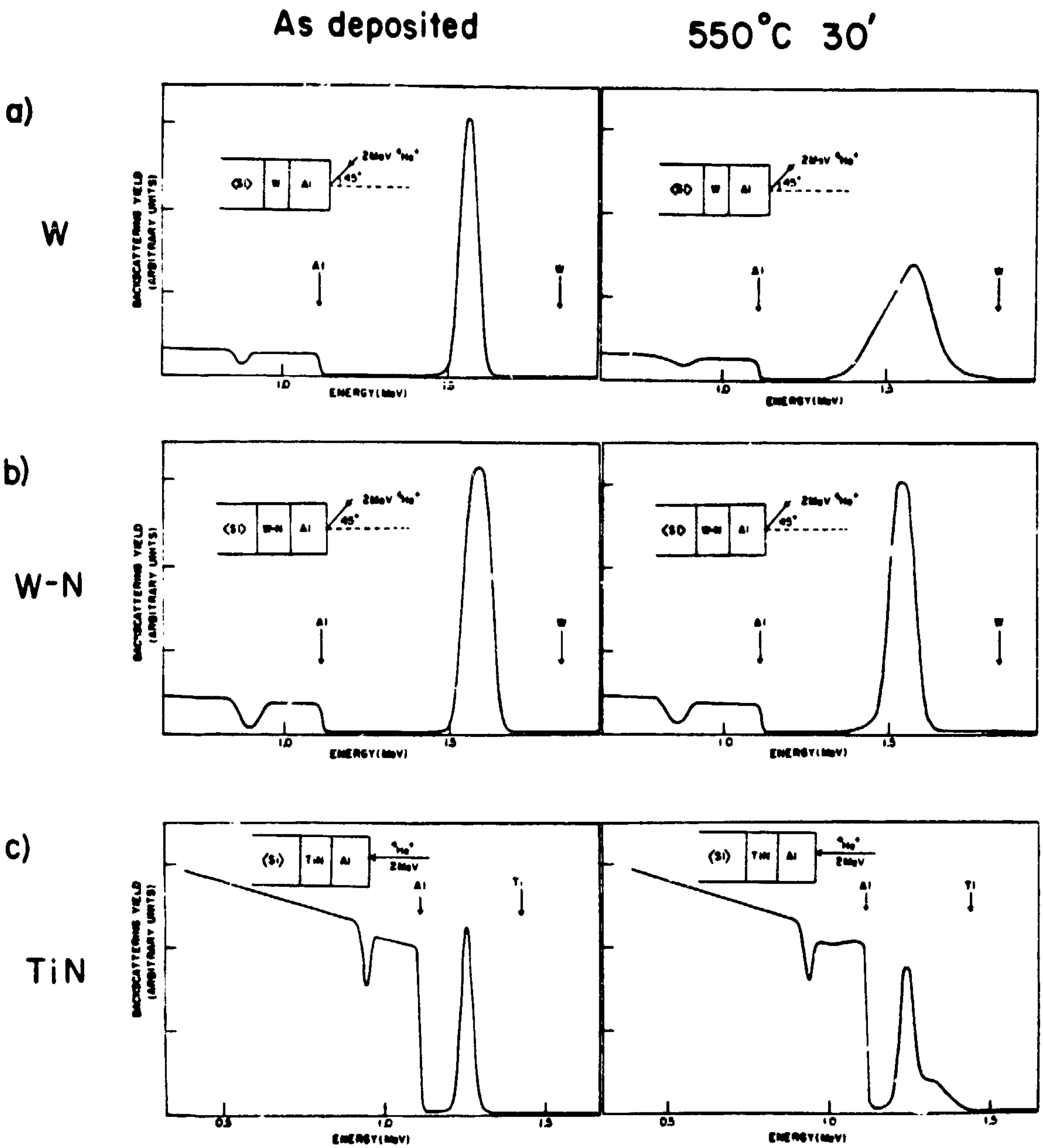
- On <100> n-type Si and SiO_2 substrates.
- R.F. sputtering, 10 mTorr (Ar + N_2), N_2 concentration: 0, 5, 10, 20, 40, 80%, 400 W, 3"ϕ; ($1 \cdot 10^{-6}$ torr vacuum).
- R.F. sputtered Al films in the same vacuum.
- Annealing in vacuum $\leq 7 \cdot 10^{-7}$ torr, 30 min.
- RBS and X-ray diffraction.

Crystallization

$\%N_2$	Crystalline Character	Crystallization Temperature
0	poly	-
5	poly	-
10	amorphous	$\gtrsim$ 500°C
20	amorphous	$\gtrsim$ 550°C
40	poly	-
80	poly	-

Barrier between Si and Al Film.

- Amorphous W-N (20% N_2) more stable than W, see Fig. 3(a) and (b).
- At 550°C, 30 min
  slight W diffusion into Si
  unchanged W-N/Al interface.


As deposited
550°C 30′
a)
W
b)
W-N
c)
TiN
BACKSCATTERING YIELD (ARBITRARY UNITS)
ENERGY (MeV)
0.5
1.0
1.5
Al
W
Ti
(Si)
W-N
TiN
2MeV
45°

Comparison With TiN

- TiN and ZrN stable between Si and Al below ~ 550°C.
- TiN and Zr-N failure may be:
  1) reaction to form compounds like $TiAl_3$ (Fig. 3(c)) or $ZrAl_3$.
  2) local stress-induced cracking.

<u>Conclusion</u>

- W-N much better than Zr-W against Al.
- W-N at least as good as Ni-N-W against Al.

Outlook

Questions: Why does N in Ni-N-W inhibit local Ni-Si reaction?

Why does N in W-N inhibit W-Al reaction?

Study W-N and W-N/Al
Zr-N
Zr-W/W-N bilayer