#### THE EMERGENCE OF PLASMA PROCESSING

M.A. Lieberman

#### Department of Electrical Engineering and Computer Sciences University of California Berkeley, CA 94720

References:

H. Abe, M. Yoneda and N. Fujiwara, Jpn. J. Appl. Phys. 47, 1435 (2008)

V.M. Donnelly and A. Kornblit, J. Vac. Sci. Technol. A31, 050825 (2013)

Special thanks to: John W. Coburn

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#### **OUTLINE**

- The nanoelectronics revolution
- The emergence of plasma processing
- The evolution of etching discharges
- Future etch challenges

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#### THE NANOELECTRONICS REVOLUTION

- Transistors/chip doubling every  $1\frac{1}{2}$ -2 years since 1959
- Billion-fold increase in performance for the same cost over the last 40 years

## EQUIVALENT AUTOMOTIVE ADVANCE

- 60 billion miles/hr (90  $\times$  speed of light!)
- 20 billion miles/gal
- 1 cm long  $\times$  3 mm wide

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#### **EMERGENCE OF PLASMA PROCESSING**

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#### HUMBLE BEGINNINGS — SILVERING MIRRORS

- Sputtering discovered by Sir William Grove in 1852
- Relative sputtering rates of various metals measured in 1890–1910
- Crude apparatus used to sputter-coat silver, platinum, etc on glass surfaces
- The mechanism of physical sputtering was not understood
- Discharge state-of-the-art in the 1920's was rudimentary

10. "NOTE ON THE PRODUCTION OF MIRRORS BY CATHODIC BOMBARDMENT"

By F. SIMEON, B.SC., F.Inst.P.

(Messrs. Adam Hilger, Ltd.)

The production of mirrors by cathodic bombardment is not a new process. Workers with vacuum tubes since Grove, 1852, have noticed the bright deposit in the neighbourhood of platinum electrodes, which is more or less marked according to the current passed through the tube and nature of the residual gas. This deposit is generally objectionable, and was especially so in the case of the older form of X-ray bulb with platinum anti-cathode. This disintegration is not peculiar to platinum, nor indeed is platinum the most easily deposited metal. Sir William Crookes in 1891 investigated the relative rates of sputtering of a number of different metals under similar conditions of discharge. The relative rates are given in the following table, in which the rate for gold is taken as 100\*

Palladium	108.80	Platinum	44.0	Iridium	10.49
Gold	100.00	Copper	40.24	Iron	5.50
Silver	82.68	Cadmium	31.99	Aluminium	0.0
Lead	75.04	Nickel	10.99	Magnesium	0.0
Tin	56-96				

Many other observers both before and since have investigated various points having some bearing upon this method. A bibliography of their papers will be found in the reference given.

A convenient apparatus consists of a vacuum tube of special form which permits of readily altering the cathode and of introducing and removing the various objects (glass plates, &c.) which it is desired to coat with a reflecting surface. The vessel employed in the apparatus exhibited is a vacuum dessicator, through the upper part of which is introduced, in addition to the exhaust tube for connection to the vacuum pump, two aluminium wires covered with glass tubing for insulation. To one of these, which is introduced centrally, can be attached a disc of the fine metal of which it is desired to form a mirror. The other, after emerging from the glass tube, is bent into a portion of a circle, in about the same horizontal plane as the surface to be coated, and so as to be as far removed from the surface as the vessel allows. These wires are connected externally to an induction coil, a Lodge valve also being included in the circuit. The article to be coated, after being scrupulously cleaned and dried, is placed upon a clean glass support in the lower part of the vessel. Connection between the two parts of the vessel is made with some form of vacuum grease, great care being exercised that neither the surface to be coated nor the cathode itself is in any way contaminated, as this will lead to some blemish in the final result. The vessel is exhausted until the cathode dark space extends nearly to the work

PLASMA

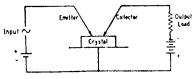
(From "The Making of Reflecting Surfaces", Phys. Soc., London, 26 Nov 1920)

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#### **INVENTION OF THE TRANSISTOR — 1948**

#### The "Transistor" – an Amplifying Crystal

THERE was a time in the early days of radio Twhen the "oscillating crystal" could be catalogued with sky hooks, left-handed monkey wrenches and striped paint, because no one knew how to amplify a signal with a galena, silicon or other crystal. All this is changed by the recent Bell Telephone Laboratories' announcement of the "Transistor," a small germanium-crystal unit that can amplify signals, and hence be made to oscillate.



Housed in a small metal tube less than one inch long and less than a quarter inch in diameter, the Transistor has no filament, no vacuum, and no glass envelope, and is made up only of cold solid substances. Two "catwhisker"-point contacts are made to a surface of the small germanium crystal, spaced approximately 0.002 inch apart.

The Transistor shown is connected as an amplifier in the accompanying sketch. The contact p on the input side is called the "conlector" and the output contact is called the "collector" by the Bell Labs. A small positive bias of less than one volt is required on the emitter, and the output circuit consists of a negative bias of 20 to 30 volts and a suitable load. The input impedance is low

(100 ohms or so), and the output impedance runs around 10,000 ohms.

In operation, a small static current flows in both input and output circuit. A small current change in the emitter circuit causes a current change of about the same magnitude in the collector circuit. However, since the collector (output) circuit is a much higher-impedance circuit, a power gain is realized. Measuring this gain shows it to be on the order of 100, or 20 db., up through the television video range (5 Mc. or so). The present upper-frequency limit is said to be around 10 Mc., where transit-time effects limit the operation.

The Bell Labs have demonstrated complete broadcast-range superhet receivers using only Transistors for oscillator and amplifier functions (with a 1N34 second detector and selenium power rectifiers). An audio output of 25 milliwatts was obtained by using two Transistors in a push-pull connection. However, it seems likely that in the nicer future Transistors will find their maximum application in telephone amplifiers and largescale computers, although their small size and zero warm-up time may make them very useful in hearing aids and other compact amplifiers.

It doesn't appear that there will be much use made of Transistors in amateur work, unless it is in portable and/or compact audio amplifiers. The noise figure is said to be poor, compared to that obtainable with vacuum tubes, and this fact may limit the usefulness in some amateur applications. These clever little devices are well worth keeping an eye on. -B. G.

QST for

October 1948

SMA

PLA

#### W.B. Shockley, J. Bardeen, W.H. Brattain

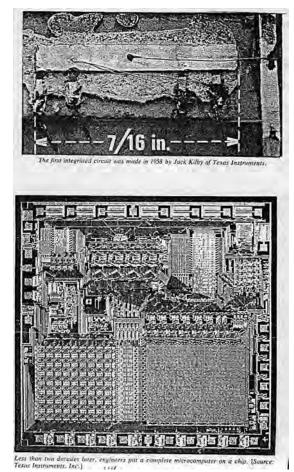
Nobel Prize in Physics (1956)

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#### FIRST INTEGRATED CIRCUIT AND MICROPROCESSOR

# Jack Kilby (1958) Nobel Prize in Physics (2000)

# Texas Instruments TMS 1000 USP 3,757,306 (1973)



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#### SPUTTER DISCHARGE STATE-OF-THE-ART — 1960's

- Parallel plate capacitively coupled rf discharges that generated energetic ions were widely used for sputter-etching and sputter-deposition
- Formation of the ion energy distribution on substrate surface
- Role of blocking capacitor and formation of self-bias voltage
- Influence of electrode area ratio on dc plasma potential
- Optical emission spectroscopy for etch end-point detection
- Reactive sputter deposition
- Basic theory of physical sputtering

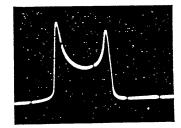
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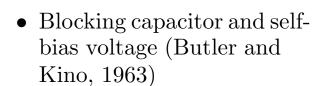
#### EXAMPLES

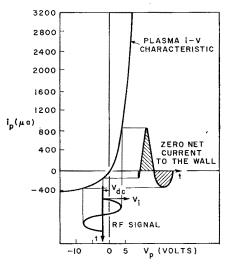
• Earliest measurement of ion energy distribution (J. Erö, 1958)

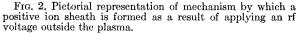
Ion flux



Ion energy







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#### PLASMA ETCH STATE-OF-THE-ART — 1970's

- Etch was isotropic
- Capacitively-powered "barrel" etchers were mainly used
- High pressures (~ 1 Torr)
- An important application was photoresist strip
- $\bullet\,$  Isotropic etching of Si, W, Ta, Ti, Si\_3N\_4 was demonstrated
- Need for volatile etch products was recognized
- No mention of energetic ion bombardment

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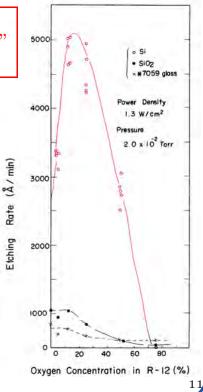
#### **ION-ENHANCED PLASMA ETCHING**

- Sputtering involatile products and high ion energies
- Plasma etching volatile products and low ion energies

Who first combined volatile products with high ion energies?

N. Hosokawa, R. Matsuzake and T. Asamaki "RF Sputter-Etching by Fluoro-Chloro-Hydrocarbon Gases" Jpn. J. Appl. Phys. Suppl. 2, Pt. 1, 435 (1974)

5	<ul> <li>Etching rate</li> </ul>	
Symbol cher		
-	Α	124 Å/min
	C <sub>2</sub> HCl <sub>3</sub>	330
R-14	CF <sub>4</sub>	900
R-11	CCl <sub>3</sub> F	1670
R-12	CCl <sub>2</sub> F <sub>2</sub>	2200
R-21	CHCl <sub>2</sub> F	410
R-22	CHClF <sub>2</sub>	1430
R-112	$(CCl_2F)_2$	1280
R-113	CCl <sub>2</sub> FCClF <sub>2</sub>	2015
R-114B2	$(CBrF_2)_2$	1850



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#### **IMPLICATIONS OF HOSOKAWA'S DISCOVERY**

(From discussions with John W. Coburn)

- The work was first presented at the Sixth International Vacuum Congress, Kyoto, Japan, 25-29 March 1974
- Hosokawa's main interest was to etch faster
- He may not have recognized the importance of his discovery for pattern transfer
- But there were many pattern transfer engineers in the audience
- In 1975, there were around a dozen "reactive ion etching" (RIE) patents filed worldwide

### ANISOTROPIC PLASMA ETCHING WAS BORN

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#### SILICON DIOXIDE AND ALUMINUM ETCHING

• Anisotropic etching of SiO<sub>2</sub> with high selectivity over Si

> R.A.H. Heinecke, "Control of Relative Etch Rates of SiO<sub>2</sub> and Si in Plasma Etching," Solid State Electronics **18**, 1146 (1975)

SiO, thermally grown	2000 %/min		
Si	≰400 <b>"</b>		
Silox densified	2000 "		
Silox phosphorus doped	3-4000 "		
Si <sub>3</sub> N4	36000 "		
Etching gas	C <sub>3</sub> F <sub>8</sub> , CP grade 99		
The second s	C.F. CP grade 90		
Pressure	0.3 torr		
Pumping speed	90 1/min		
Leak rate	<0.01 torr/min		
Susceptor	Stainless steel, water cooled.		
Plasma current density	6mA/cm <sup>2</sup>		

• Anisotropic etching of Al with native Al<sub>2</sub>O<sub>3</sub> etch

S.I.J. Ingrey, H.J. Nentwich, and R.G. Poulsen "Gaseous Plasma Etching of Al and Al<sub>2</sub>O<sub>3</sub>" USP 4,030,967 (filed 1976)

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#### **EVOLUTION OF ETCHING DISCHARGES**

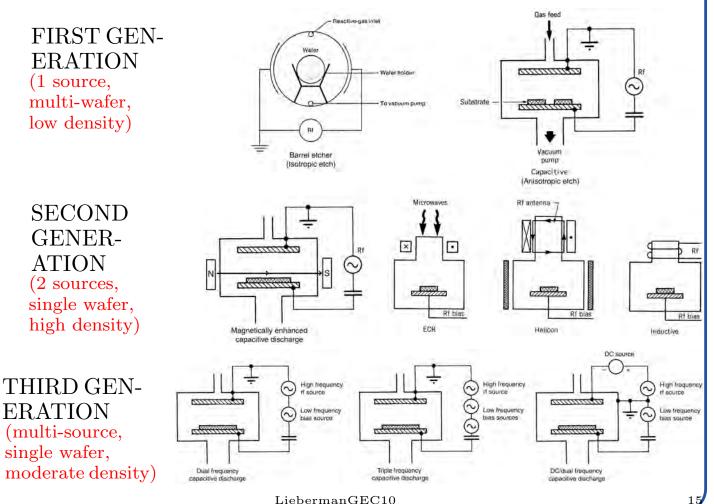
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#### THREE GENERATIONS OF ETCHING DISCHARGES

FIRST GEN-ERATION (1 source,multi-wafer, low density)



- PLASMA

#### HIGH DENSITY INDUCTIVE DISCHARGES

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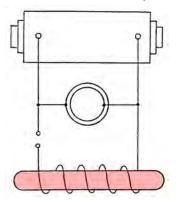
### MOTIVATION

- High density (compared to capacitive discharge)
- Independent control of plasma density and ion energy
- Simplicity of concept
- RF rather than microwave powered
- No source magnetic fields

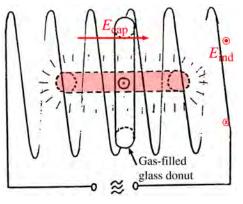
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#### EARLY HISTORY

• First inductive discharge by Hittorf (1884)



• Arrangement to test discharge mechanism by Lehmann (1892)

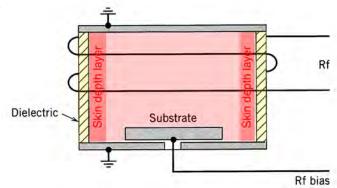


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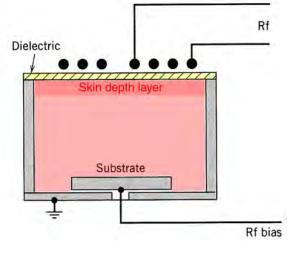
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#### CYLINDRICAL AND PLANAR CONFIGURATIONS

• Cylindrical coil



• Planar coil



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# MICROWAVE DISCHARGES, PULSING, AND ELECTRONEGATIVE GASES

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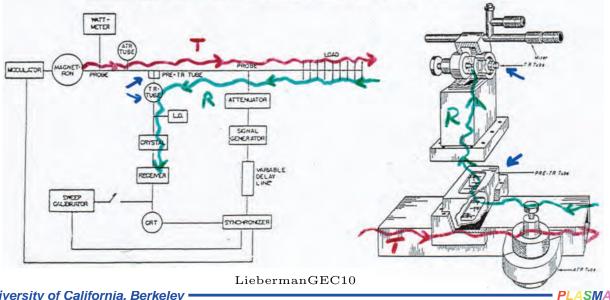
#### HIGH DENSITY PULSED MICROWAVE DISCHARGE

PHYSICAL REVIEW SEPTEMBER 1 AND 15. 1940 VOLUME 70, NUMBERS 5 AND 6

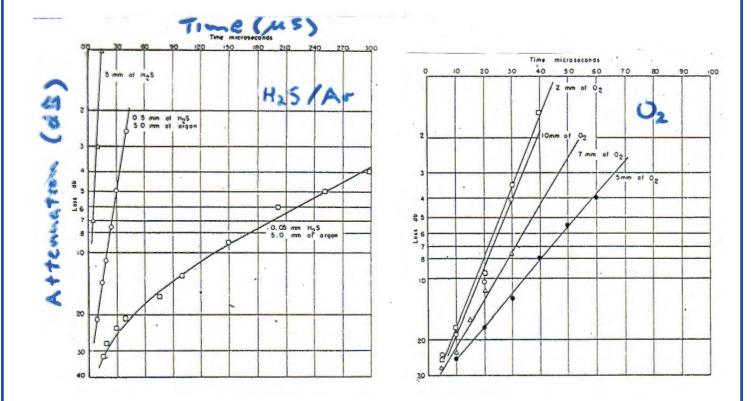
#### Physical Processes in the Recovery of TR Tubes1

H. MARGENAU,<sup>2</sup> F. L. MCMILLAN, JR.,<sup>3</sup> I. H. DEARNLEY,<sup>4</sup> C. S. PEARSALL<sup>5</sup> AND C. G. MONTGOMERY<sup>2</sup> Radiation Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts (Received May 3, 1946)

Gas-filled switching (TR) tubes are important components of a radar duplexer. The recovery of the tube, i.e., the elimination of ions on termination of the discharge, is of great interest because it determines the quality of radar reception. In the first part of this paper, techniques of measurement of the recovery of certain types of TR tubes are described and results are reported. In the second part, the physical processes responsible for recovery are discussed in connection with simple theoretical developments concerning recombination of electrons and positive ions, diffusion of electrons, and capture of electrons by gas molecules. The last of these processes is found to be of principal importance in removing electrons and producing a short recovery time.



## ELECTRONEGATIVE DISCHARGES (Ar/H<sub>2</sub>S, O<sub>2</sub>)



• Attaching gases soak up electrons fast

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#### FUTURE ETCH CHALLENGES

- New materials and structures
- For 10 nm CD, must control accuracy to  $\pm 1$  nm (1.8 lattice constants!) across 450 mm wafer  $\Rightarrow$  Gentle and precise etches

## **RESPONSES**

- Evolutionary: more "knobs" on "existing" tools
  - Multiple driving frequencies/dc/magnetic fields etc
  - Segmented electrodes/driving coils/chucks etc
  - Many pulsing duty cycles, frequencies etc

 $\Rightarrow$  Tight control of electron, ion and photon energy distributions and fluxes

• Revolutionary: atomic layer etching and neutral beam etching

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