High-purity Platinum for Microelectronics

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The introduction of the transistor has had an impact on the electronic industry of gigantic proportions. Those associated with the development and rise of transistorised electronics are keenly aware of the stringent purity requirements placed on the silicon and germanium semiconductor materials. For most impurity elements, the concentrations must be less than one part per billion and for many, less than one part in 10^{11} host atoms. The need for high purity semiconductor materials was the primary impetus for development of ultrapurification techniques such as the zone refining process.

The current revolution in electronics has been brought about by the incorporation of the transistor element with the entire circuit on the same silicon wafer or chip. These "integrated circuits" consist of interconnected circuit elements (resistors, capacitors, conductors, amplifiers, etc.) in the form of thin films inseparably associated on the same substrate, and in a minute space such that as many as 600 individual circuits can be produced on an area the size of a silver dollar.

A variety of metals are utilised for integrated circuit components. Although the purity required may not be as demanding as that for the silicon substrate, many metallic components are either in direct contact with the silicon or separated by only thin ($< 10^{-4}$cm) layers of oxides (or other metal layers) such that diffusion of certain impurity elements into the silicon must be guarded against. Of particular significance are the alkali metals, which in concentrations of one part per million, can destroy the electrical properties of the device. Consequently, high purity enhances device yield and reliability. Since there are between 100 to 200 manufacturing steps in the process, the attainment of a satisfactory overall yield is a major problem.

Platinum is used in integrated circuit fabrication as an intermediate layer between an interconnecting gold layer and a protective silicon nitride layer. The platinum prevents the diffusion of gold into the silicon nitride and subsequently into the silicon layer. In addition, a thin (0.05 micron) platinum layer is initially sputtered on the silicon wafer and reacted to form a platinum silicide layer on the terminal ends of the wafer. This platinum silicide forms a good low-resistance ohmic contact to the silicon. A completed monolithic integrated circuit is depicted in Fig. 1, and a layered section is shown in Fig. 2.

Purification

A wide variety of processes are used to purify metals. Since most metals occur in nature in the form of compounds such as oxides or sulphides, generally the first step is to separate the metal from the non-metal by some type of a reduction process. Beyond that, further purification may include chemical precipitation from solution, chemical vapour deposition, distillation or sublimation processes and electrolyses.

The ultimate in purity for most metals has been attained by a liquid phase technique called zone refinement. The zone melting process was originally developed by Pfann and his co-workers at Bell Telephone Laboratories (1, 2). It was first applied to silicon and germanium in order to provide high purity semiconductor materials for transistor devel-

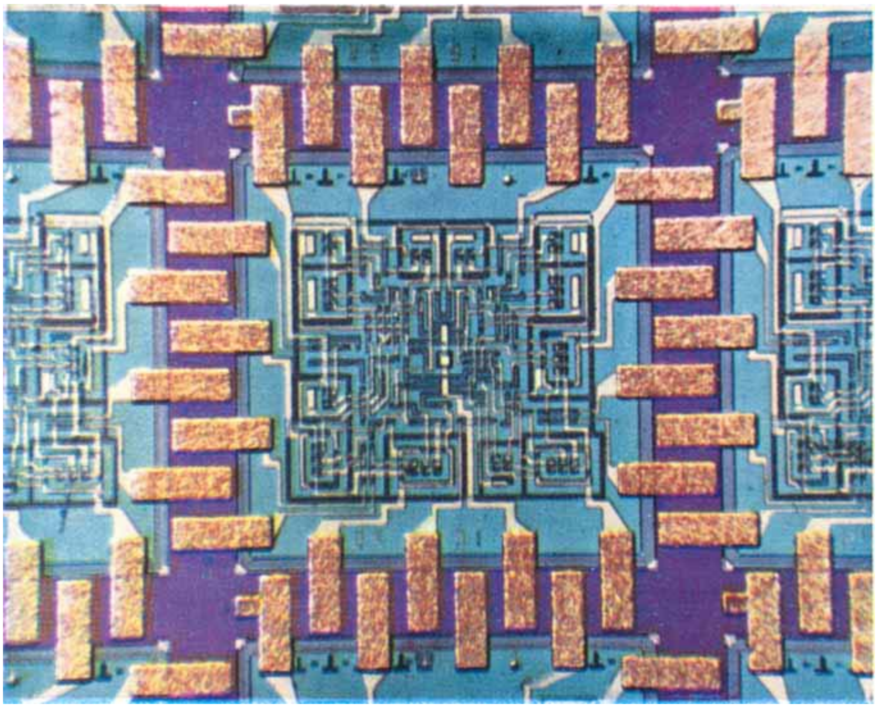

Fig. 1 A completed beam-lead monolithic integrated circuit. Each polished silicon wafer 150–200μ thick can hold of the order of 600 integrated circuits. (Courtesy of Western Electric Eng., *December 1967.)*

opment. In this process purification is dependent on the difference in solubility of the impurity elements between the liquid and solid phase. A molten zone is made to move very slowly (e.g., 2 in/h) along a bar of metal. Those impurity elements more soluble in the liquid than in the solid tend to move with the liquid. (Most impurity elements are more soluble in the liquid phase.) By moving this zone a number of times in one direction, impurity elements are piled up at one end of the bar. This end section is removed and discarded (or in the case of platinum used for applications where purity is less important).

It has been shown (2) that the solute concentration C_s in the solid at a distance x from the starting end after one zone pass is a function of the initial concentration, C_o, the molten zone length l, and the effective distribution coefficient k as follows:

$$C_S/C_O = 1 - (1 - k) \exp[-kx/l]$$

The distribution coefficient is a function of the ratio of the solubility of the impurity element in the solid to that in the liquid.

Metals and semiconductors were first zone refined by placing a suitable bar in a long boat or crucible. Later the floating-zone technique was introduced (3), in which the metal was suspended in a vertical position and the molten zone was held in place by the metal's own surface tension. This somewhat limited the diameter of bar that could be refined but had the distinct advantage that the material being refined did not come into contact with a crucible and thus could not become contaminated by the latter.

The Electron Beam Heat Source

Several types of heat sources have been employed to achieve the molten zone, the most common being induction heating, resistance wire wound furnaces, radiation heating and electron bombardment. The last-mentioned source has become the most popular method for zone melting the higher

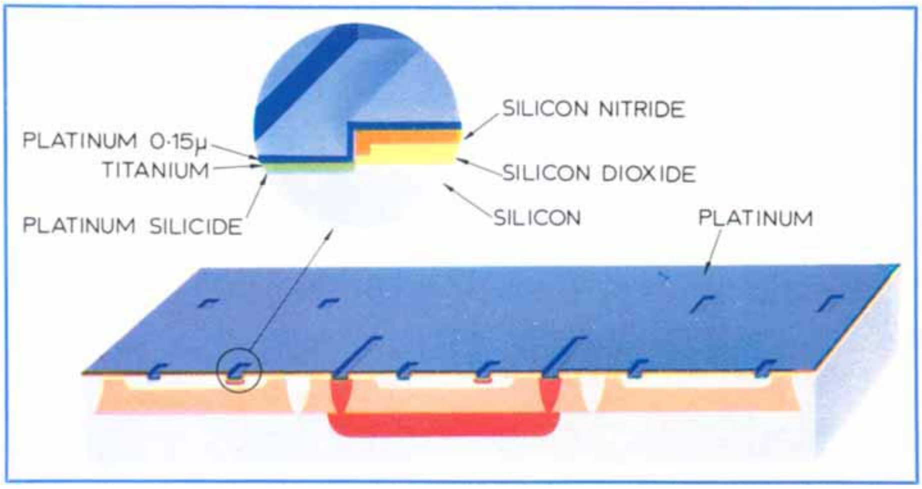

Fig. 2 Cross section of part of a crystalline silicon wafer after deposition of platinum. Typically there are between 100 and 200 stages in the complete process of integrated circuit manufacture. (Courtesy of Western Electric Eng., *December 1967.)*

melting-point metals. In this technique, electrons which are emitted from an annular filament surrounding the rod material are accelerated toward the rod by virtue of a high d.c. potential. The kinetic energy of the electrons is converted to thermal energy on striking the target. Electron bombardment offers two principal advantages over the other techniques, namely the low power required and the ease of control of the molten zone configuration. For example, less than 1 kW is required to produce a molten zone in a ½-inch diameter platinum rod, compared to 5 to 10 kW for typical induction units. By use of electrostatic focusing shields the electrons can be confined to a small region, and thereby produce a small well-controlled molten zone which is especially desirable for the maintenance of a floating type zone. This molten zone is made to move slowly along the length of the rod specimen. In order to maintain the electron beam, the entire operation must be conducted in a vacuum of 10^{-4} torr or less. Although this may be a disadvantage for a few high vapour pressure metals, the high vacuum required plays a major role in the purification process for most electron beam floating zone operations. An electron beam system is shown in Fig. 3.

The Role of the Vacuum System

In addition to purification by zone melting *per se*, in vacuum melting purification also occurs by:

(*a*) degassing, i.e., the removal of oxygen, nitrogen and hydrogen, as well as CO or CO_2 formed by side reactions of oxygen with carbon;

(*b*) vacuum distillation of high vapour pressure elements.

The removal of gaseous elements takes place initially by virtue of the change in solubility in the liquid with the partial pressure of the same elements in the surrounding media. This was experimentally verified for partial pressures of a few hundred millimetres of mercury by the early experiments of Seiverts (4) leading to the well-known relationship

$$S \approx \sqrt{P}$$

where S = the solubility of gas in the liquid phase, and

P = the partial pressure of the same gas in the surrounding media.

This purification process is dependent on the ability of the vacuum system to maintain a sufficiently low gas partial pressure near the molten surface, on the diffusion of the gas atom through the liquid to the surface, on the

Fig. 3 An electron beam float-zone refiner. The platinum rod is given three vertical zone-refining passes at a zoning speed of three inches per hour

presence or absence of any stirring action that might enhance the gas atom transport in the liquid phase, and on the composition of the starting material.

Vacuum distillation is a purification process based on the preferential evaporation of solute. To a first approximation, the degree of purification is dependent on the ratio of the vapour pressure of solute to that of the solvent. In addition to this ratio, it is essential that the vapour pressure of the solute be high relative to its partial pressure in the

Mass Spectrographic Analysis of Three-pass Zone-refined Platinum

Element	Content (weight) (ppm)	Element	Content (weight) (ppm)	Element	Content (weight) (ppm)	Element	Content (weight) (ppm)
Li	<0.0002	V	0.25	Ru	0.3	Dy	<0.01
Be	<0.02	Cr	2.5	Rh	15.0	Ho	<0.003
B	0.0003	Mn	0.6	Pd	0.6	Er	<0.008
C	10.0	Fe	3.0	Ag	0.012	Tm	<0.003
H_2	1.5	Co	0.3	Cd	<0.025	Yb	<0.06
O_2	10.0	Ni	2.5	In	0.03	Lu	<0.003
N_2	3.0	Cu	0.05	Sb	<0.004	Hf	0.05
F	<0.003	Zn	0.05	Sn	0.08	Ta	<5.0
Na	<0.06	Ga	0.01	Te	<0.008	W	5.0
Mg	<0.06	Ge	<0.004	I	<0.002	Re	<0.02
Al	7.0	As	0.01	Cs	<0.002	Os	<0.08
Si	7.0	Se	<0.003	Ba	<0.003	Ir	0.3
P	0.002	Br	0.008	La	<0.002	Au	<0.3
S	0.2	Rb	<0.01	Ce	<0.002	Hg	<0.15
Cl	0.4	Sr	<0.003	Pr	<0.002	Tl	<0.15
K	0.1	Y	<0.01	Nd	<0.01	Pb	<0.6
Ca	0.05	Zr	2.5	Sm	<0.01	Bi	<0.06
Sc	<0.03	Nb	1.0	Eu	<0.005	Th	<0.07
Ti	2.5	Mo	<0.3	Gd	<0.01	U	<0.07
				Tb	<0.003		

immediate vicinity of the molten surface. As the solute content at the liquid/vapour interface becomes diminished, a concentration gradient is set up within the liquid. At this time, and this may occur very early in the melting operation, material transport in the liquid phase becomes the rate-controlling process. Thus, providing the vapour pressures are favourable and that the pumping speed of the vacuum system is sufficient to maintain a low partial pressure of the solute element, purification should proceed at a rate dependent on the solute diffusivity in the liquid state.

Resulting Purity

An electron beam floating-zone refiner is shown in Fig. 3. Platinum purified in this unit at Materials Research Corporation is zone melted in a nominal 10^{-6} torr vacuum system. The metal rod of $\frac{3}{8}$ to $\frac{1}{2}$ inch diameter is given three zone passes at a zoning speed of 3 inches per hour. It has been found that most of the purification by the degassing and vacuum distillation mechanism occurs during the first zone pass. For appreciable purification by zone melting *per se*, a minimum of three zone passes should be utilised. Although zoning beyond three passes is beneficial, it has been found that three passes is a good compromise between purity and cost of processing.

A detailed analysis of a three-pass zone-refined platinum bar is given in the table. The residual concentration of the interstitial gases – hydrogen, oxygen and nitrogen – is very low. The content of the other metals of the platinum group and of gold and silver has been reduced to very small proportions in general. Platinum of the purity indicated in the table is now very satisfactory for use in microelectronic applications and the zone refining technique described in this article gives good results.

References

1 W. G. Pfann, "Zone Melting", *Metall. Rev.*, 1957, **2**, 29

2 W. G. Pfann, "Zone Melting", John Wiley & Sons, New York, 1958

3 H. C. Theuerer, *Trans. Metall. Soc. AIME*, 1956, **206**, 1316

4 A. Seiverts, *Z. phys. Chem.*, 1911, 77, 591

Rhodium-Platinum Thermocouples for Incinerator Control

The disposal of the ever-increasing volumes of household and trade refuse is presenting local authorities with a considerable problem. Incineration under controlled conditions is a practical solution being adopted by a number of authorities (1). At Middleton, Lancashire, Motherwell Bridge Tacol Ltd has installed for the local Corporation the first incinerator of an advanced design which can handle 60 tons of refuse per day at the rate of 8 tons per hour.

Incoming refuse is fed from a hopper to the incinerator grate, which consists of six rollers arranged in descending order at an angle of 30°. Each roller is made up into a unit 8 feet wide and 5 feet in diameter from interlocking grate bar segments between which gaps allow fan-forced combustion air to pass. The rollers slowly rotate and refuse is dried and ignited as it falls from one roller to the next until it finally leaves the grate as fine ash and clinker. Incinerator temperature is monitored and maintained at 900°C by a Petite Q12 indicator/controller fed with signals from a duplex platinum : 10 per cent rhodium-platinum thermocouple in the roof of the combustion chamber.

After leaving the last roller the ash and clinker is quenched in a submerged belt conveyor and is passed on for disposal. The hot flue gases pass via a dust extractor to a 150 foot chimney. A second duplex platinum : 10 per cent rhodium-platinum thermocouple monitors the flue gas temperature at the entrance to the dust extractor and passes a signal to control the introduction of cooling air to the gas stream.

1 *Instrum. Prac.* 1969, 23, (10), 706–707