Ces premières études sont encourageantes, tant au point de vue technologique (prise de spectres d'échantillons d'environ 100 nm d'épaisseur), qu'au point de vue résultats. Nous pensons poursuivre afin de tenter de mieux interpréter les phénomènes de transformation de carbone en graphite.

En conclusion, il semble que la Mole permette de solutionner plus ou moins complètement des problèmes posés dans différents domaines des sciences de la Terre.

Tous les exemples présentés ont été traités en utilisant la Mole se trouvant au laboratoire de M. Delhaye à Lille et sont destinés, avec d'autres, à faire une sorte de bilan ou de mise au point sur l'apport d'un appareil tel que la Mole dans les sciences de la Terre.

Ce travail a bénéficié de l'aide financière de la D.G.R.S.T. (Action concertée n° 78-07-0824) et des collaborations au B.R.G.M. de M. Picot, de M$^{\text{elle}}$ Oudin, de M. Sureau, de M. Cécile, de M. Massal.

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Applications of Raman microprobe analysis to manufacture of semiconductor devices

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Application de l'analyse par microsonde Raman dans la fabrication de semiconducteurs

La technologie courante de l'industrie des semiconducteurs produit des systèmes avec une grande densité de circuits, circuits dont les dimensions sont mesurées en microns. Une contamination par particule, pendant le traitement, peut entraîner des courts-circuits ou des circuits ouverts dans le système : et, pour cette raison, il est essentiel de connaître la composition de tels contaminants afin de trouver leurs sources. Les méthodes de microanalyse classiques, comme la microscopie électronique à balayage (SEM), l'analyse à la microsonde électronique et la spectroscopie Auger donnent une information par élément plutôt que par molécule et elles détruisent l'échantillon. Puisque beaucoup de problèmes de contamination sont de nature organique, on a trouvé que la microsonde Raman était un excellent instrument d'analyse.

En plus des problèmes de contamination par particules, la microsonde Raman a été utilisée pour des mesures de distribution de matériaux à l'intérieur d'un substrat céramique sur lequel le « chip » du microcircuit fini était monté. Cette analyse inclut l'étude de l'interaction entre le substrat céramique et les pâtes métalliques qui forment les conducteurs sur la surface du substrat. Une autre application concerne les problèmes qui apparaissent pendant le processus de raccord des « chips », dans lequel des contacts électriques sont établis entre le « chip » et les conducteurs métalliques du substrat.

Integrated circuit technology is a method by which a large number of electrical circuits are placed on small silicon chips of a few millimeters square dimension. Technological advances now require geometrical tolerances of the order of micrometers for the circuit elements. Particulate contamination control therefore becomes a critical concern in the manufacture of such devices. Such contamination is frequently organic in nature; spectroscopic analytical techniques are the only practical means of identification.

By repeated operations such as masking, etching, diffusion, evaporation, etc., an array of several hundred replicated chips are built up on a silicon wafer. At each operation the wafer becomes more valuable, and yield losses become more critical. The final processing steps, in which the individual chips are joined to substrates for electrical communication with the « outside world », are referred to as « packaging ». This report discusses some problems of packaging for which the Raman microprobe has been used to identify the presence of foreign material, or to analyze material composition in a very small area.

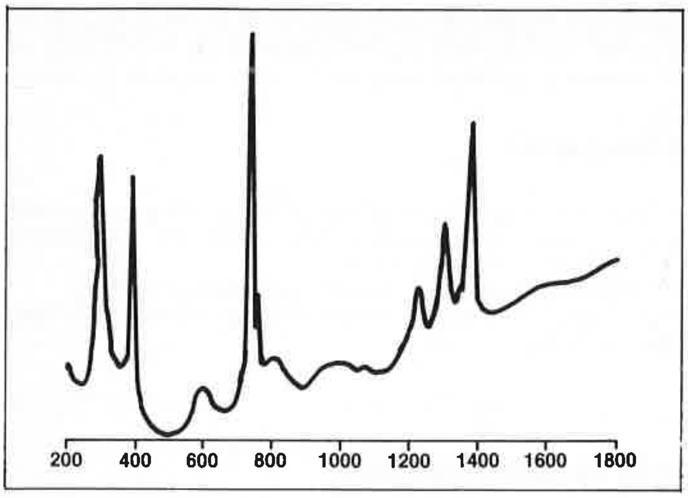
In order to provide electrical connections between the chip circuits and the supporting substrate, Sn/Pb solder balls are deposited on the chip. A perforated molybdenum mask is used to deposit the solder at the proper positions on the wafer. Occasionally some of the holes (100 mm diameter) become plugged, preventing solder deposition, and consequently the corresponding chips must be rejected. Raman microprobe analysis revealed the presence of a plastic resin with the holes; the analysis was complicated by the burning and melting of the material in the laser beam, and it was necessary to operated at reduced laser power.

After the solder balls are in place, the wafer is diced by means of circular cutting blades to form the individual chips. The wafer is mounted into an adhesive tape backing to hold the chips in place during the cutting operation. We have found that the spinning blades will carry adhesive from the back surface to the top surface of the chip, and have used microprobe analysis to identify the material as adhesive.

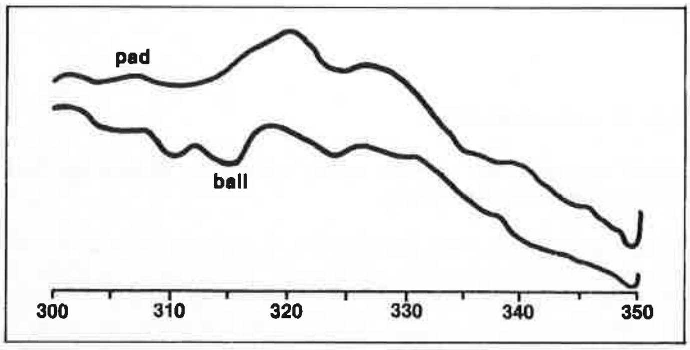
In the chip-joining operation, the chip is positioned on the ceramic substrate and placed in a furnace. The solder balls melt and electrical connections are thereby formed. Sometimes a solder ball does not wet the conductor pad and the resistance of the join is too high. We have identified small amounts of a corrosion product of tin of unknown stoichiometry, best described as SnO_xCl_y with those joins which have failed. In another instance we have found growths of lead oxide, PbO, on the solder balls of devices after storage.

For some devices, a copper ground plane is placed over the metal conductors on the ceramic substrate. It is insulated from the conductors by a Teflon (poly-perfluoropropylene) film. The plane laminate is held in place by wires spot-welded to it. White material appearing at the spot-weld sites was identified by microprobe analysis as Teflon.

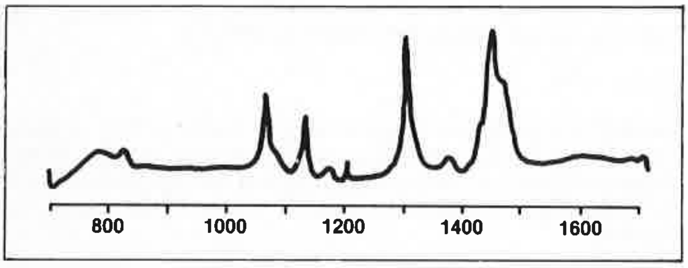
In the new technology of multi-layer ceramic (MLC) substrates, electrical wiring between different chips on the same substrate is achieved by means of metal conductors in stratified layers within the laminated ceramic structure. The caramic is formed from glass frit and alumina (Al_2O_3), with a polymer and plasticizer for binder. The mixture is formed into a slurry with solvents, and is cast into a continuous film and dried. The resulting « green sheet » is then punched and metal pastes are screened into it. A number of green sheets are stacked together, and fired at high temperature to form a rigid ceramic structure. During the firing, the green sheets shrink due to loss of binder, and it is necessary that all sheets in the structure



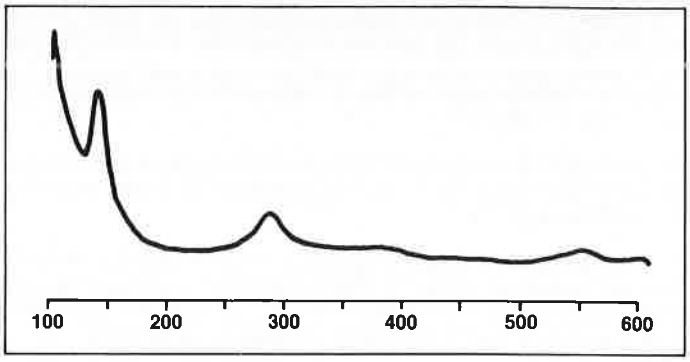
Ground plane weld deposit Teflon $(CF_2)_n$



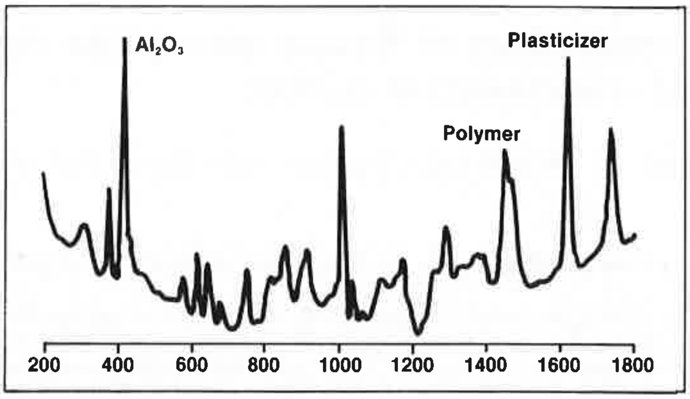
Solder corrosion product (SnO_xCl_y)



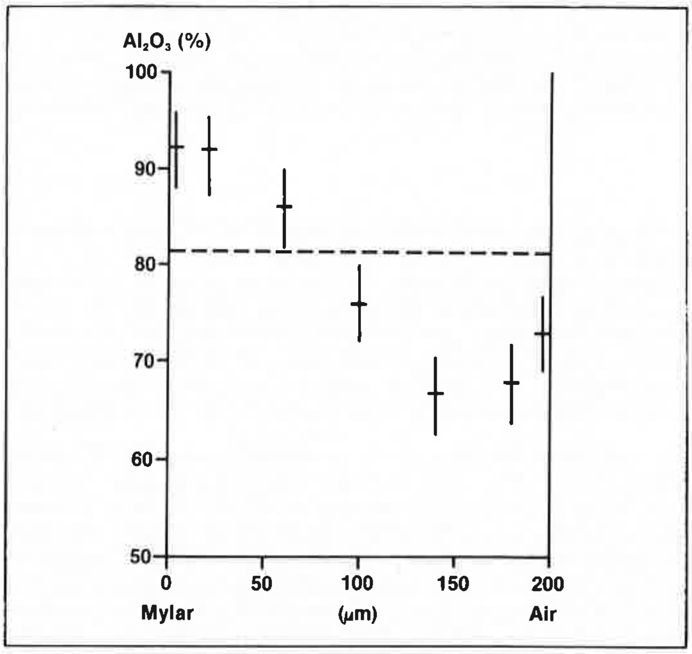
Molybdenum mask contamination



Solder ball deposit (PbO)



Air side of green sheet composite



Distribution of Alumina in green sheet

shrink uniformly, so that registration of metal patterns between adjacent layers is maintained.

During the casting operation, solvent evaporation causes the polymer and plasticizer binder to partially separate from the alumina and glass, so that the top and bottom surfaces of the green sheet are different in composition. We have been able to show this compositional distribution by microprobe analysis. Since the laser beam size under the microscope is comparable to the alumina particle size, we observe a point-to-point variation in composition along the surfaces. Using a large beam diameter, in a standard 90° scattering chamber, we can average out the local compositional variation. In this way we can study the effect of process variables, such as casting temperature, on the composition of the green sheets. We have also been able to profile the composition across an edge of the sheet (about 200 µm thickness), and we find that the gradient is not linear, but instead the alumina concentration undergoes a minimum within the sheet.

During certain operations on the MLC module, the surfaces are overlaid with a protective film of Mylar (poly ethyleneterepthalate), which is later removed. We have been able to show that some Mylar remains on the ceramic surface (but not on the metal surface) after the film is removed. The amount of residual Mylar is highest at the edges of the MLC, and is lowest in the center. There is also a shift in band positions between the free film and the residual Mylar, indicating some sort of bonding interaction between the polymer and the ceramic.

In each of the above examples, Raman microprobe analysis has yielded valuable information which would be difficult or impossible to obtain in any other way. Our instrument has been in operation less than a year, and we are confident that with our operating experience it will continue to be an essential analytical tool for trouble-shooting problems unique to semiconductor device manufacturing.