SMALL AREA MOLECULAR ANALYSIS AS APPLIED IN THE MICROELECTRONICS INDUSTRY

J. Ramsey

To cite this version:

<10.1051/jphyscol:19842202>. <jpa-00223879>

HAL Id: jpa-00223879

https://hal.archives-ouvertes.fr/jpa-00223879

Submitted on 1 Jan 1984

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
SMALL AREA MOLECULAR ANALYSIS AS APPLIED IN THE MICROELECTRONICS INDUSTRY

J.N. Ramsey

Z41C, IBM, Hopewell Junction, NY 12533, U.S.A.

ABSTRACT

Small area elemental analysis techniques have been successfully applied to the solution of microelectronics development and manufacture for 24 years. Molecular analysis would be far more useful if it could be done in device sized areas. Several such techniques, infrared, Raman, polarized light microscopy and laser/mass spectroscopy will be discussed and their usefulness illustrated for organic contamination, including skin. The Leybold-Heraeus LAMMA 1000, when the laser power to the specimen is kept very low and reproducible, gives fragmentation spectra which are recognizable as those by electron impact mass spectroscopy, on which most/all library searches are based.

INTRODUCTION

It has been 24 years to the month since Prof. David Wittry presented the first application of the electron probe microanalyzer to the solution of semiconductor/microelectronics problems. The need for small area chemical analysis has been strong in this field because of continuing miniaturization. This small area analyses, almost exclusively elemental, have been essential for process development and problem solving. Elemental information, however, is often not sufficient, for example, getting hydrogen, carbon, oxygen and nitrogen on a particle does not add measurably to its identification and elimination from a process.

Polarized light microscopy has long been used in chemical and mineralogical studies, and was raised to a high level of applicability by Walter McCrone and associates, culminating in the extensive Particle Atlas, which included innumerable glasses, organics and polymers.

Small area molecular spectroscopies were obviously desirable, but there were problems of coupling a microscope and a spectrometer and retaining high energy transfer. This was solved for Raman by Delhaye and Dhamelincourt, which resulted in 1 micron lateral resolution Raman capability in an instrument (the MOLE) produced by Jobin-Yvon. This technique has been widely applied, including the field of microelectronics. Small area infrared analysis was made possible with the introduction of the Nanometrics 2018. We have applied this extensively to process control problems in microelectronics manufacturing. The use of the visible in Raman to see infrared transitions offers advantages.

Laser desorption/ionization and mass analysis has been available in the transmission mode for several years in the LAMMA 500 by Leybold-Heraeus. This technique has recently been extended to the much more useful reflection mode as the LAMMA 1000 by Leybold Heraeus18,20 and the LIMA by Cambridge Mass Spectroscopy Co.21 It is evident that one of the major parameters to be controlled and measured is the laser power, to get reproducible fragmentation, hopefully recognizable to an organic mass spectrosocptist and close to those from electron impact, so that extensive literature/libraries can be utilized. If the laser power is too high and fragmentation extends to H, C, O and N, then little molecular information is obtained, of course.
EXAMPLES OF PROBLEM SOLVING BY MOLECULAR ANALYSIS

I. Particles on Recording Surface
One of our development lines had a problem, with ~10μm particulate contamination on a recording surface, which caused "dropped bits" on reading, and subsequent re-writing. In-situ small area Raman analysis (top two spectra of Figure 1) showed the material to be polypropylene (comparing it with the bottom spectrum). Polypropylene, we were told, was not a possible contaminant because there was no polypropylene in the materials of construction or packaging. A further look at the problem revealed the material was used to clean the surface on command. This material was "teased" apart and examined microscopically (insert Figure 2). There are small nodules on the fibers, seemingly helping to hold the fibers together. The fibers were shown to be cellulose by conventional infra-red analysis, but by polarized light techniques, the nodules were distinguished to be polypropylene by small area Raman (third spectrum, Figure 1) and by small area infra-red (Figure 2). Was this indeed the source of the polypropylene particles? We could not be sure, because while this was the only known source, there were no distinguishing elements unique to these polypropylenes (electron microprobe and LAMMA showed it, but that is the usual catalyst in polypropylenes). The "proof" came when a different vendor's filter paper (without nodules of any type) was used without subsequent problems.

What difficulties did we encounter with these analyses? The particles were embedding small area and were difficult to remove, giving fragments which were difficult to collect together on an infra-red transparent substrate for small area infra-red: it failed. The fibers (approximately 10μm) were too small for small area infrared, and masses were too thick; it failed. LAMMA fragmented the fibers and nodules too much; it failed (see later for LAMMA successes).

II. Particulate Analysis: Is it Nylon or Skin?
Nylon and human skin are very common contaminants in clean rooms (and not-so-clean rooms, too). The Nylon comes from garments and bushings/gears, while humans are constantly exfoliating skin flakes and fragments. We had great success with small area infrared, and small area Raman fibers. However, as R.M. Scott has pointed out, Nylon and skin are both amides, their infrared spectra are quite similar, requiring full width at half maximum for differentiation. Raman and polarized microscopy were explored as improvements, with the latter being especially successful. The very high bi-refrangement of drawn Nylon (1.580 index of refraction) with 1.520 transverse, coupled with its distinctive hemispherical form with dimpled craters after melting (~265°C) allows unequivocal differentiation from skin, with its low bi-refrangement (~1.530 index of refraction). In addition, the oils and salts in skin outgas at room temperature (and especially after ~265°C).

III. LAMMA 1000 Analyses
As mentioned earlier, the degree of fragmentation of a molecular ion controls the amount of useful information to lead to a molecular analysis, and I mentioned two examples of excessive fragmentation. This precise control and measurement of very low laser power applied to the specimen is essential. Frank Anderson of IBM and Hans Heinen of Leybold-Heraeus have worked out such a method, and it will be discussed in their future paper. They were kind enough to provide some of their early results on known organic materials, which enabled them to identify an unknown material within the scope of this present paper, namely small area molecular analysis applied to micro-electronic device fabrication problems.

The attempt was to get LAMMA fragmentation reproducible and to be recognizable to an "organic" mass spectrometrist, by controlling and measuring the low laser power applied to the specimen. Three sample materials, well characterized by Electron Impact/Mass Spectroscopy were chosen: Benzophenone, an aromatic ketone (Fig. 3), Rhodamine B, an indicator dye (Fig. 4) and Poly Alpha Methyl Styrene, an unzippable polymer (Fig. 5). These LAMMA "successes" (defined as recognizable to EI/MS) gave confidence to try an unknown, a residue discovered after an etching and cleaning process showed the material to be the aromatic sulfonic acid. (Note the overlap of the two mass range spectra, with 157 on both.)

CONCLUSIONS
While there are several small area molecular analysis techniques, they are usually complementary, with more than one required for a full analysis and solution to process problems: there is no universal technique.

ACKNOWLEDGEMENTS
I am indebted to my colleagues for sharing their data and ideas: F.W. Anderson - IBM; D.L. Falcon - Small area polarized light analysis; H. Heinen (Leybold-Heraeus) - LAMMA analysis; K.P. Madden - Small area and conventional infra-red analysis; C.D. Needham - Small area Raman analysis; R.M. Scott - Small area infra-red analysis; C.E. Wilson - Small area infra-red analysis.
RAMAN SPECTRA OF PARTICLES ON RECORDING SURFACE

Fig. 1. Raman Spectra of Particles, Nodules and Polypropylene Film

Fig. 2. Infra-red Spectrum of Nodules

Fig. 3. Negative Spectrum of Benzophenone by LAMMA 1000

The protonation would be pressure sensitive and may not occur at very low laser power, giving 182 as in EI.
NEGATIVE SPECTRUM FROM LAMMA 1000

Fig. 4. As indicated, all EI mass peaks are found in LAMMA, along with many extraneous peaks, which might confuse a novice mass spectroscopist, but experienced organic mass spectroscopists can "see" the pertinent peaks. This points out the high level background required in the early(?) stages of any analytical/characterization technique, for organics, especially.

POLY ALPHA METHYL STYRENE
Unzippable polymer

Fig. 5
SPECTRA FROM LAMMA 1000

RESIDUE AFTER ETCHING & CLEANING
NITROBENZENE SULFONIC ACID
C₆H₅NO₅S
M=203

Fig. 6

NEGATIVE SPECTRA
203 Parent (M)

157 M-NO₂
173 M-N₃
C isotope peaks

REINEN/ANDERSON IBM