

Lumière blanche (transmission)

100 μ



Fluorescence ($1\ 000\ \text{cm}^{-1}$)

Figure 4. Photographie de motifs de résine réalisées sur microsonde Raman.

matériau. L'image de la raie Raman à $523\ \text{cm}^{-1}$ montre par contre que les bandes sont du silicium. A cause de la petite taille des motifs il n'a pas été possible de faire l'image Raman avec l'éclairage annulaire, ce qui explique que l'on ne voit un contraste que sur la partie centrale de la photo, correspondant à la surface du spot d'analyse.

Discussion des résultats

La microsonde Raman et la sonde de Castaing donnent des images du silicium avec une résolution comparable en première approximation, on observe sur les deux photographies un élargissement notable de la bande de silicium. Notons enfin que la microsonde Raman permet de dire que l'élément silicium est sous forme de silicium cristallisé alors que la sonde de Castaing montre peu de contrastes entre du silicium pur et de l'oxyde de silicium par exemple.

2. Ces mêmes bandes recouvertes de $100\ \text{nm}$ de SiO_2 thermique

Le deuxième échantillon était identique au précédent, mais le silicium présentait en surface un oxyde de $100\ \text{nm}$. La sonde de Castaing montrait la présence d'oxygène aussi bien dans les barreaux de silicium que dans le substrat d' Al_2O_3 . Il est donc impossible de savoir, quant au signal oxygène, quelle est la contribution de SiO_2 et celle de Al_2O_3 . La méthode n'est pas adaptée.

La microsonde Raman a été également infructueuse : le pic des liaisons Si-O était trop faible.

3. Des motifs de résine HPR 104

Le dernier échantillon concernait la visualisation de motifs de résine HPR 104. Il n'a pas été trouvé en sonde de Castaing d'élément en concentration suffisante pour faire une image. En effet l'hydrogène n'est pas détectable et la mesure du carbone est très délicate sur les appareils classiques.

En microsonde Raman, nous avons dû nous contenter d'une image de fluorescence présentées sur la figure 4.

Conclusion

La mole et la sonde de Castaing sont deux outils voisins, complémentaires pour l'imagerie des couches minces utilisées lors de la fabrication des circuits intégrés. La microsonde X a l'avantage de donner un signal pour tout matériau (à l'exception des éléments légers). La microsonde Raman présente l'avantage de donner une information sur la liaison chimique, donc à la fois la nature de l'élément comme la microsonde X, mais aussi son état chimique.

Raman, photoluminescence and cathodoluminescence as complementary small area analytical techniques

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Raman, photoluminescence et cathodoluminescence comme techniques complémentaires pour l'analyse de petites zones

La cathodoluminescence (CL) a été utilisée dans le passé pour la caractérisation des composés phosphorescents et a été étendue à d'autres matériaux dans les 15 dernières années. Notre intérêt pour cette technique, chez I.B.M., a été suscité par ses possibilités comme moyen de caractérisation de petites zones pour les circuits intégrés, complémentaire des travaux de la sonde électronique de microanalyse et de diffraction des rayons X/électrons. Quelques-uns des problèmes et résultats de la CL ont été présentés par Marty Mitchell et moi-même à la conférence MAS, à Miami Beach et à Boston (1, 2).

Le micro-Raman est une technique de caractérisation de petites zones pour lesquelles sont obtenues des informations sur la liaison atomique/moléculaire. Il se révèle être une extension naturelle de notre répertoire des techniques d'analyses complémentaires des petites zones et surfaces (3).

Cet article explore les possibilités et avantages de la technique micro-Raman (particulièrement de la Mole de Jobin-Yvon) et étend ses opérations dans le domaine de la photoluminescence (PL) en

comparant, avec la CL, les mêmes échantillons. Des exemples : nitrure de bore, MgO , Al_2O_3 (avec additions d'alliage), codérite (alpha et mu), films minces de garnets, sont exposés et discutés.

Similitude et différence de ces techniques sont également discutées.

(1) J. N. Ramsey et M. J. Mitchell « Cathodoluminescence studies of various Aluminas at low kV »; Late news paper, 11th Ann. Conf. Microbeam Analysis Society, Miami Beach, FL (août 1976).

(2) M. J. Mitchell et J. N. Ramsey « Difficulties of interpreting cathodoluminescence spectra of bulk and thin film ionic materials », présenté à Microbeam Analysis Society Meeting, Boston, MA, août 1977; VIIIth International Conf. on X-Ray optics and microanalysis.

(3) J. N. Ramsey, « Micro-Raman, photoluminescence and cathodoluminescence as complementary techniques »; Late news paper at Microbeam Analysis Society, Annual Meeting, San Antonio, TX (15 août 1979).

Introduction

Boron nitride would be a difficult material for small area analysis by microprobe as the X-ray emission wavelengths are so long. Thus optical spectroscopic techniques with a small beam are very attractive. There are at present two excitation modes, viz. laser with a microscope to focus the light, or an electron beam. There are at present two emissive modes possible, namely Raman (which is related to IR, and therefore to molecular bonding) and photoluminescence (PL)/cathodoluminescence (CL) (which sees electron band/gap/trap energies).

All Raman and photoluminescence (PL) were made using the Mole, which has been described in detail earlier in this workshop. Raman scattering is related to the same vibrational modes seen in IR, but is

seen as the difference (Delta) between the wave number of the mode and the wave number of the laser line, this Delta being in the visible. The laser line is selected and filtered through either a blue or green narrow bandpass « spike » filter to get either the Ar Blue ($20\,492\text{ cm}^{-1}$; 487.9 nm) or Ar Green ($19\,436\text{ cm}^{-1}$; 514.5 nm). These filters lose their effectiveness about 100 nm outside their center point and it is necessary to use a broad band-pass filter, centered about either 487.9 nm or 514.5 nm in tandem with the « spike » filter to eliminate the rest of the argon spectra above a Delta of about $3\,500\text{ cm}^{-1}$. One can readily convert Delta to wavelength for any laser line : figure 1 shows conversion curves for the Ar Blue and the Ar Green.

Cathodoluminescence (CL) measurements are made with a 1/4 meter Jarrell-Ash monochrometer attached to the optical microscope on

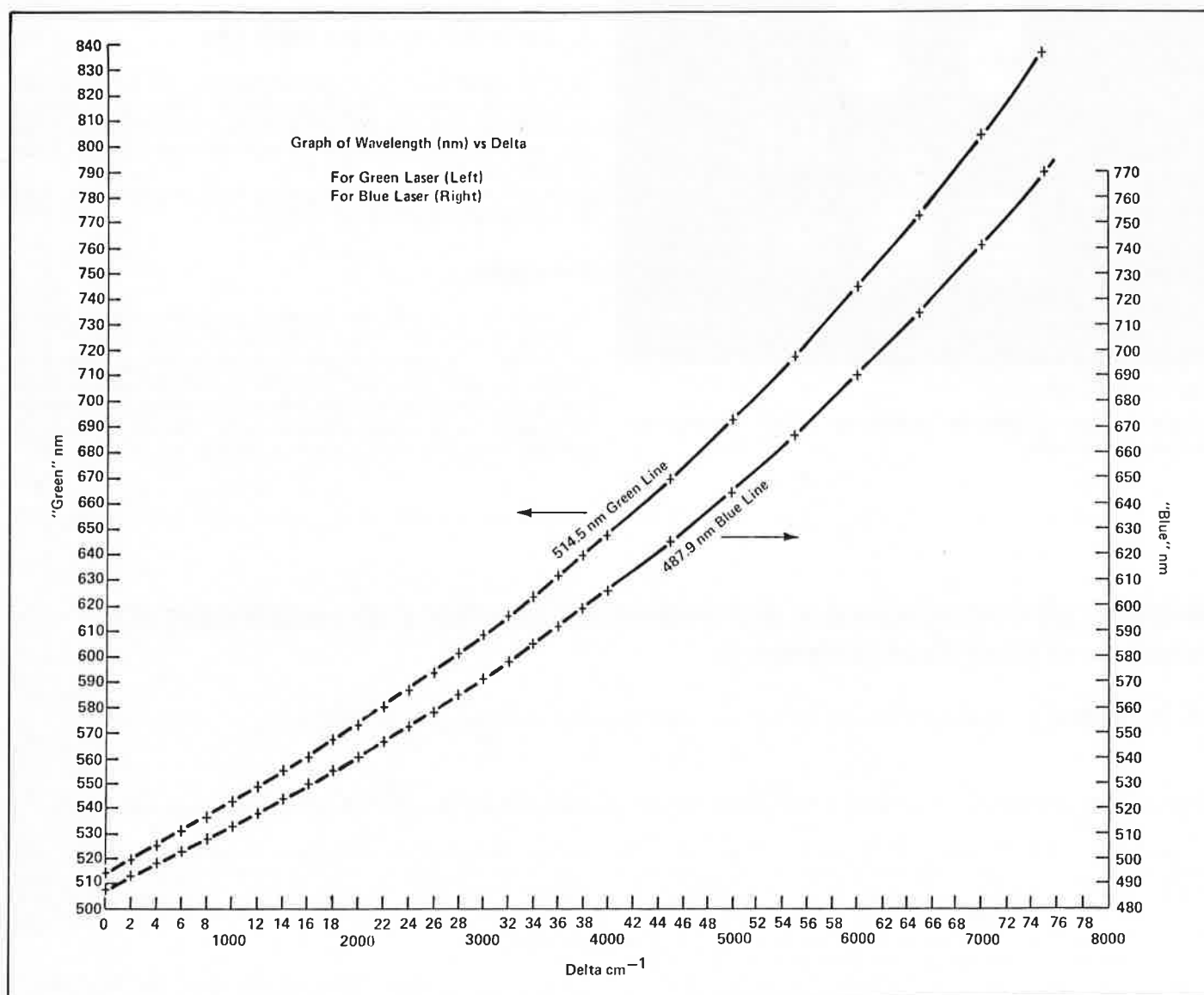


Figure 1.

an Applied Research Laboratory electron microprobe following the design of Knisely, Laabs and Fassel (1). It is possible to work with a 2-3 μ beam. CL studies have been reported elsewhere (2, 3). Photoluminescence and cathodoluminescence must be interpreted in terms of the electron band gap/trap/defect structure of the atoms and therefore are influenced by many things, e.g. temperature, Vegard's Law, stress, quasi-particles, and even trace quantities of transition elements.

Applications

While the talk showed applications of these three optical spectroscopy techniques in seven materials (See abstract), only two will be discussed here because of space constraints.

Alpha and Mu Cordierites

Alpha and Mu cordierites are magnesium aluminum silicate crystalline phases which can precipitate from various complex ceramic or mineral systems. While they are listed as identical composition ($Mg_2Al_4Si_5O_{18}$), they are different crystal structures according to the ASTM and JCPD cards (the Alpha being a « stuffed » orthorhombic and the Mu being a « stuffed » hexagonal Beta quartz structure). Another small area characterization technique is required because :

- 1. The crystals encountered in microstructures are usually smaller than X-ray diffraction spatial resolutions (even our 10 μ m with a Rigaku Denki Microdiffractometer).

- 2. Their compositions wouldn't be differentiated by X-ray spectroscopy in SEM or electron probe microanalyzer. Figure 2 shows the PL and CL of Alpha and Mu cordierites. The main feature in PL is in a sharp doublet at 694-695 nm which is luminescence from an impurity level (optical emission showed ~ 2000 ppm Fe) similar to the Cr^{3+} ruby laser line in Al_2O_3 . There are variations between α and μ in the smaller peaks, with the most prominent difference being the 686-688 in the α : this would allow identification and mapping of α vs. μ crystallites larger than 1-2 μ . The poorer resolution CL spectra do not reveal differences between α and μ , but do reveal the impurity luminescence rising out of the broad CL peaks.

Gadolinium-gallium garnets

Garnets constitute a wide class of materials. Our main interest in these materials is for magnetic bubble memories, which are built with an epitaxial layer of magnetic garnet grown on a non-magnetic garnet substrate.

$Gd_3Ga_5O_{12}$ has become a largely universal substrate material and is grown commercially in single crystals, 6-8-10 cm in diameter and are processed and handled like Si for semiconductor devices. Raman of a 1978 $Gd_3Ga_5O_{12}$ substrate is shown in figure 3 and is seen to be a rich spectrum. The extremely intense lines suggested that they might not be Raman lines but may indeed be photoluminescence lines. This figure includes the use of Argon Green (top) and Argon Blue (bottom) and as Raman line location are independent of the frequency of the incoming light, it is possible to separate and assign values to the Raman and photoluminescence (PL) peaks. In the talk,

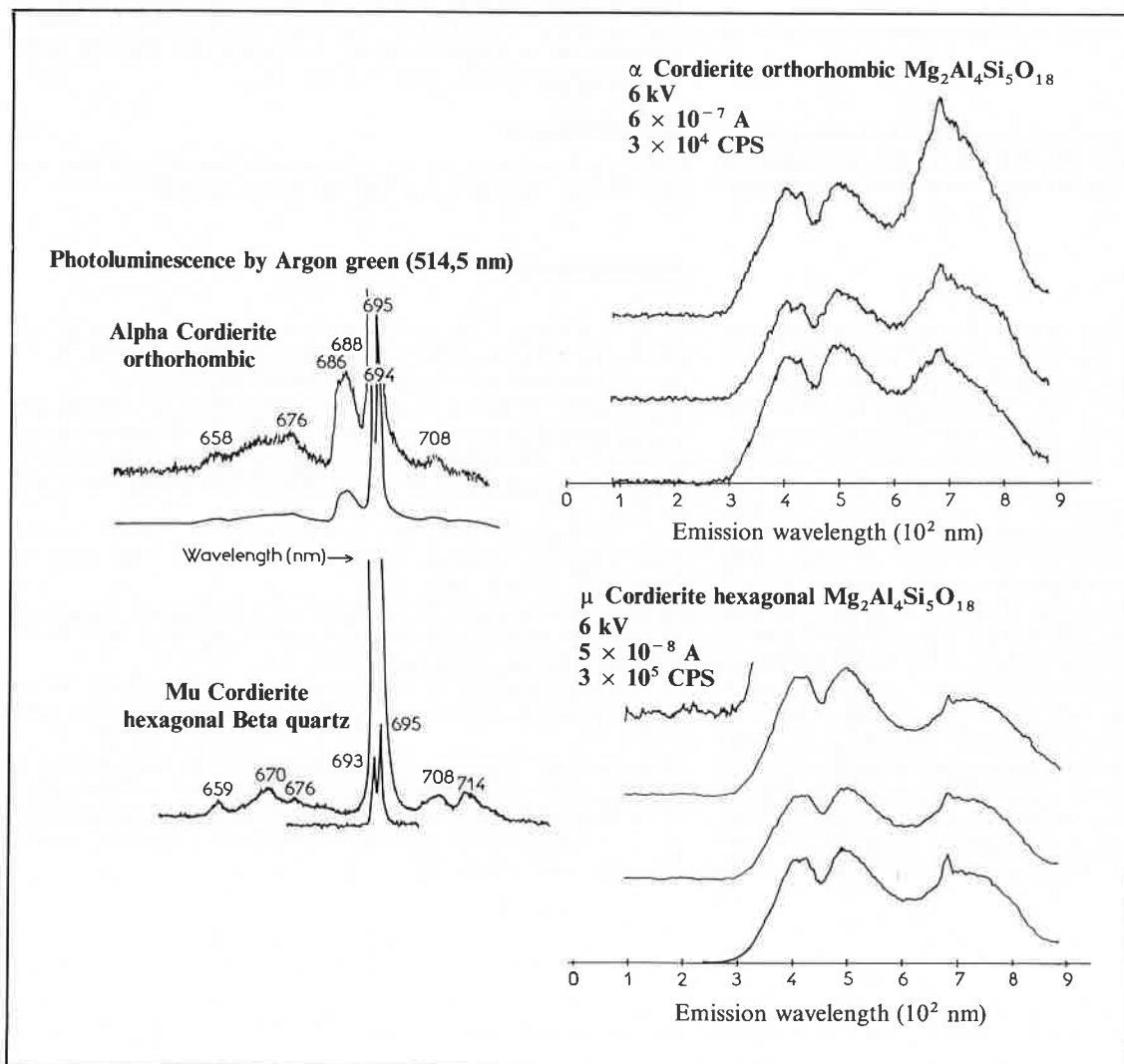


Figure 2.

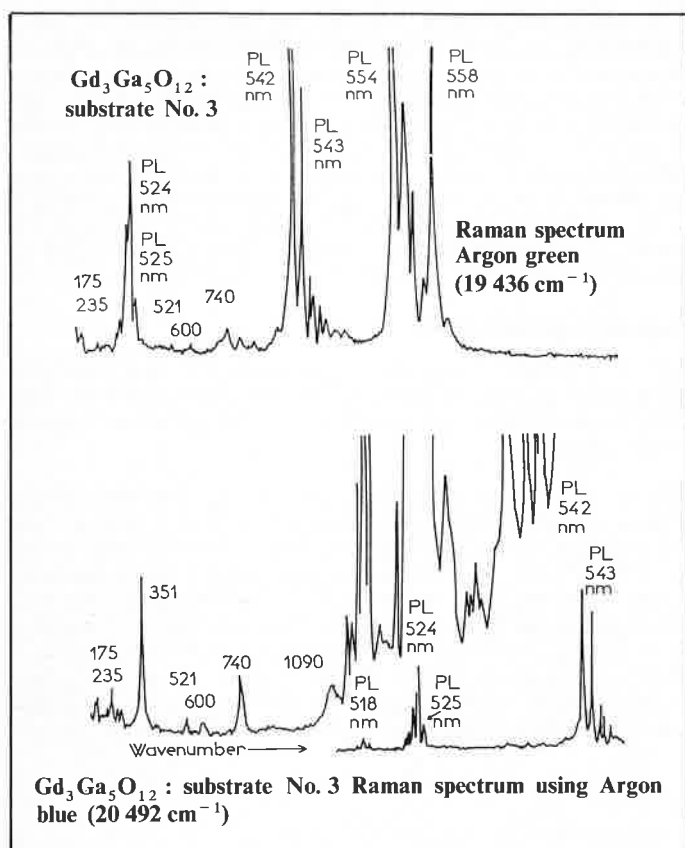


Figure 3.

I showed the wide variations in Raman and PL with different garnets, so that Raman and PL will be useful techniques to characterize small areas which show variations in magnetic properties, for example.

Discussion and plans

It will require a great deal more spectral and chemical analysis and understanding to establish the limits of PL and CL, e.g. while photoexcitation is controlled by selection rules (and exceptions), excitation by an electron beam is not. This is the first thought on the reason that BN and MgO show CL but not PL, because we aren't populating the excited state. It is evident with the impurity luminescence of $\text{Al}_2\text{O}_3 : \text{Cr}$ and cordierite : Fe that the peak/background of PL on the Mole is superior, to that of CL. This may be inherent in the two processes, but may also be mainly due to the wide differences in the optical spectrometers in the two systems, viz. 1 meter, with concave holographic grating and stray light rejection on the Mole vs. 1/4 meter, with flat grating on the ARL microprobe (this difference would certainly account for the better resolution on the Mole). The trade-off is time, for the PL spectra are ~ 45 min. each vs. ~ 2 min. each for the CL spectra. I will shortly be installing a Tracor-Northern DARSS rapid scan spectrometer for both CL and PL, which will allow the faster luminescence rise and fall times to be followed, and will allow signal averaging. Charles Needham, who uses our Mole for organic Raman analysis primarily has already added a Nicolett 535 Signal Averager. In addition, the needs for lower temperature have long been noted, and the problems of cold stages for the ARL microprobe and the Mole are being

addressed. Commercial lasers further into the UV are being explored to extend the range of PL to shorter wavelengths. As seen in figure 3, PL can be unique whereas CL, with its lower resolution at present isn't a qualitative technique for identifying a material (3).

We plan to follow-up with further work on α and μ cordierites, including detailed X-ray diffraction. α and μ , of the same composition but with different crystal structures (α is orthorhombic and μ is hexagonal β quartz); the structures themselves are highly distorted (« stuffed ») and give the same « d » spacings with the exception of one line. The line intensities are different, however, indicating differences in structure factors, which in turn are related to the location/distribution of the atoms on the diffracting planes. This may be the key to molecular bonding relating to the marked differences in the Raman scattering from the two materials.

Conclusion

We've seen a « pot pourri », a « bouillabaise » of examples of the information possible by using these three complementary small area techniques. The use of an electron microprobe for the CL offers the secondary advantage of doing X-ray analysis on the same region. Another complementary small area technique is microdiffractometry which can allow a full X-ray diffraction phase and stress analysis on regions as small as 8-10 nm in diameter (Walker, ref. 4).

There are other exciting possibilities for stress analysis in certain materials in 1-2-3 nm diameter region because, e.g. in Si, the Raman peak (520.2 cm^{-1}) splits into a triplet under uniaxial stress (Anastassakis, ref 5) and the Cr^{3+} luminescence line shifts under stress in Al_2O_3 (6) and MgO (7). Raman, photoluminescence and cathodoluminescence provide excellent small area characterization techniques to complement X-ray diffraction and electron probe micro analysis in many classes of materials.

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