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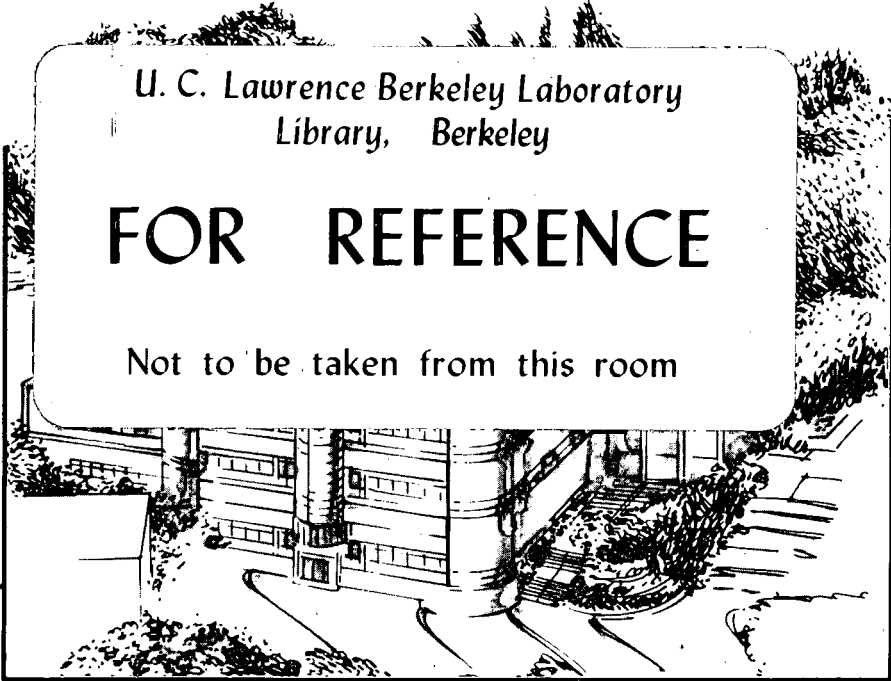
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## Profiling and Mapping of Advanced Materials using Spatially Resolved Raman Spectroscopy

J.W. Ager III, D.K. Veirs, H.Q. Lee, and G.M. Rosenblatt

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**Profiling and Mapping of Advanced Materials using Spatially  
Resolved Raman Spectroscopy**

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## PROFILING AND MAPPING OF ADVANCED MATERIALS USING SPATIALLY RESOLVED RAMAN SPECTROSCOPY

J.W. Ager III, D.K. Veirs, H.Q. Lee, and G.M. Rosenblatt

We have developed a technique to profile important physical and chemical properties of materials based upon simultaneous acquisition of Raman spectra along a laser illumination line, coupled with extensive and rapid spectral analysis to extract the desired information. The technique uses a two-dimensional spectroscopic detector and, in contrast to Hadamard techniques, sample movement in one dimension that allows all collected light to be detected. Property maps comprised of the analysis results of more than 10,000 Raman spectra can be built up from successive profiles in a few hours. In order to increase efficiency, the data for one profile are analyzed while the data for the next profile are collected. Two recent applications are discussed: measuring spatial variations in crystalline quality in CVD-grown diamond thin films and mapping transformed zones produced by compressive stress in a bulk sample of phase-stabilized zirconia (PSZ).

### Experimental

The spatially resolved Raman technique has been described previously.<sup>1,2</sup> As shown schematically in Fig. 1, a cw laser is focused on the sample by a cylindrical lens to form an illuminated line, which is imaged by the collection optics onto the entrance slit of the monochromator. The dispersed light is collected by a two-dimensional detector (1024×1024 wavelength × distance pixel format). Each row contains the entire Raman spectrum from the corresponding point along the illuminated line on the sample. The spectra are analyzed individually in real time to obtain the property of interest. The information obtained from the simultaneously acquired spectra produce a one-dimensional profile across the sample of chemical or physical

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properties that are distinguishable by their Raman spectral features. Sample translations perpendicular to the illumination line, along with repeated collection and analysis cycles, allow two-dimensional maps to be generated. The measured maximum spatial resolution and spectral precision are  $5\ \mu\text{m}$  and  $0.16\ \text{cm}^{-1}$ , respectively.<sup>1</sup>

In the diamond measurements, the magnification of the collection optics was  $8\times$ , such that each row on the detector corresponded to the Raman spectrum from a  $3\ \mu\text{m}$  long ( $25\ \mu\text{m}$  pixel size/8) by  $15\ \mu\text{m}$  wide ( $120\ \mu\text{m}$  spectrometer entrance slit width/8) area of the sample. The laser power at the sample was  $150\ \text{mW}$  and the collection time was  $1.5$  hours. Diamond peak frequencies and widths were computed for each spectrum (each row) in the data matrix by fitting a Lorentzian lineshape to the spectrum with a linear background term.

The Raman peaks in the spectrum of MgO-PSZ are broad and the changes in the sample occur over a distance scale of mm. Therefore, the maximum spatial and spectral resolution were not needed, and the data were collected in a  $256\times 256$  reduced image format (row and columns summed together in groups of four) to reduce the collection and analysis time. The magnification of the collection optics was  $1.8\times$ , such that one image row corresponded to a  $55\ \mu\text{m}$  ( $25\ \mu\text{m}\times 4/1.8$ ) by  $90\ \mu\text{m}$  ( $160\ \mu\text{m}$  slit width/1.8) area on the sample. Each spectrum (each row) was analyzed by fitting the observed spectrum to previously measured spectra of pure monoclinic and pure tetragonal zirconia. The spectral region used for the analysis included the  $149$  and  $266\ \text{cm}^{-1}$  peaks of tetragonal zirconia phase and the  $181$  and  $190\ \text{cm}^{-1}$  peaks of monoclinic phase zirconia. A map was built up using a translation step length of  $0.5\ \text{mm}$ . The collection time for each profile was  $10$  minutes. Fifteen profiles were collected for a total mapping time of  $2.5$  hours;  $2535$  spectra were analyzed.

### Sample preparation

The diamond samples studied here were grown by microwave-plasma-assisted chemical vapor deposition (CVD). The plasma used to grow sample 2C3 was smaller than the  $10\ \text{mm}$  diameter Si substrate. As a result, film growth was inhomogeneous. Scanning electron microscope (SEM) images of 2C3 show isolated, higher quality, faceted microcrystals in the center of the film and fused, lower quality, rounded microcrystals toward the edge. Sample 5W7 is a  $200\ \mu\text{m}$  thick free-standing film. The SEM images of 5W7 show uniform growth.

The zirconia sample is a 25 mm diameter hemisphere of commercial MgO-PSZ that was subjected to a two hemisphere compression test [Fig. 3(b)].<sup>3</sup> One of the hemispheres cracked almost exactly in half, forming the 25 mm diameter quarter sphere studied here.

### Results and Discussion

Chemically synthesized diamond films have all of the attractive properties of natural diamonds such as hardness and high thermal conductivity; current and proposed applications include heat sinks, X-ray optics, tool coatings, abrasives, and high-band gap semiconductors. Current research is concentrating on refining the processing to produce higher quality films and to increase the growth rate. Raman spectroscopy is the single most valuable tool presently available for the evaluation of diamond film quality; observation of the characteristic Raman line at  $1332\text{ cm}^{-1}$  is definitive evidence of diamond growth. The focus of this work is to gain atomic-scale information from the frequency and shape of the diamond Raman line and then to relate this to the important physical and mechanical properties of the film.

The one-dimensional spatial profiles of Raman linewidths and frequencies of samples 2C3 and 5W7 are shown in Fig. 2. For sample 2C3, the analyzed region extended from the center of the sample toward the edge. For sample 5W7, the region extended from the edge 1.6 mm toward the center of the rectangular piece. The Raman characteristics of sample 2C3 show continuous changes as a function of position. The diamond linewidth is narrowest near the center of the sample (where SEM showed better crystalline quality) and increases monotonically towards the edge of the sample (where SEM showed worse crystalline quality). In sample 2C3, shifts in the Raman frequency correlate with increases in the linewidth; the line frequency is  $1332.7\text{ cm}^{-1}$  in the center of the sample and increases to  $1334.4\text{ cm}^{-1}$  at the edge of the imaged area, while the linewidth increases from  $7$  to  $14\text{ cm}^{-1}$ . Sample 5W7 does not show systematic changes in the Raman spectrum as a function of position. The average frequency and linewidth of the diamond Raman peak are  $1332.5\text{ cm}^{-1}$  and  $5.1\text{ cm}^{-1}$ .

The correlation of linewidth and frequency with film quality and with each other suggested by these spatially resolved spectra is interesting because linewidth and frequency are affected by different underlying physical factors. For example, the peak frequency is affected by strain (related to stress or temperature), while a peak is either homogeneously broadened by a decrease in phonon



lifetime, or heterogeneously broadened by simultaneously sampling sample regions with different Raman frequencies, or both. In these experiments, as discussed in detail elsewhere,<sup>4</sup> shifts in the Raman peak frequency away from  $1332.5\text{ cm}^{-1}$ , the peak frequency of single crystal diamond, are attributed to stress in the films. Compressive stress shifts the peak to higher frequency, while tensile stress shifts the peak to lower frequency. The stresses probably are introduced during the cooling of the film from the growth temperature (typically  $900^\circ\text{C}$ ). The Raman linewidth of single crystal diamond is  $2\text{ cm}^{-1}$ ; the linewidths of the films studied here are larger ( $5 - 15\text{ cm}^{-1}$ ). The broadening arises from a decrease in domain size caused by defects and by a stress distribution among in the many microcrystallites sampled in a Raman measurement. The stress gradient is probably primarily in the direction perpendicular to the film.

Phase stabilized zirconias are members of a new class of fracture-resistant ceramics based upon the discovery that the stress-induced martensitic transformation from the tetragonal to the monoclinic phase occurs in fine  $\text{ZrO}_2$  grains subject to stress fields in the vicinity of a propagating crack. The degree of toughening is related to the spatial extent and the amount of transformation of the transformed zone. For a complete understanding of these materials, a quantitative measure of the extent of transformation (spatial and amount) is required. Because the spectra of the tetragonal and monoclinic phases are easily distinguished, spatially resolved Raman spectroscopy can be used to measure the relative fraction of monoclinic phase as a function of position.<sup>2,5</sup>

In other work, we have studied fatigue cracking in a variety of PSZ systems.<sup>2,5</sup> Here, we study a PSZ sample cracked by steady state loading. The two hemisphere compression test discussed above and depicted in Fig. 3(b) is used to simulate powder compaction in studies of powder metallurgy.<sup>3</sup> A map of the fraction of monoclinic phase near the contact point of the PSZ quarter sphere is shown in Fig. 3(c). Along the sphere axis there is a 1.5 mm region of 100% transformation of tetragonal to monoclinic phase and a 1.7 mm region of partial transformation. The transformed zone does not extend beyond 3.2 mm from the contact point. The transformed zone is approximately symmetric around the sphere axis. Work is in progress to compare the mapping results to the predictions of elasto-plasticity and crack propagation models.

### Conclusions

Spatially resolved Raman spectroscopy allows one to obtain unique information not available from other characterization methods. This type of information can be of great use in commercial processes as well as in fundamental research. In the production of CVD diamond films for commercial applications, high quality films with spatial uniformity may be of paramount importance. Spatially resolved Raman spectroscopy is a practical method to measure quality and uniformity simultaneously in these films. In fundamental research, the large number of spectra one can collect and analyze allow one to observe correlations which are not readily noticed with single-point techniques. Understanding complex behavior in modern materials requires spatial information. In PSZ, Raman maps of phase composition are, at present, the only quantitative measure of the size and extent of the phase-transformed zones produced during fracture or under stress that lead to improved mechanical properties in these materials. Spatially resolved imaging of chemical or physical properties based on spectroscopic data has resulted in increased understanding of complex modern materials.

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#### Figure Captions

FIG. 1 Schematic of illumination geometry for spatially resolved Raman spectroscopy.

**FIG. 2** Profiles of diamond Raman frequency and linewidth across two CVD diamond films. Each profile was obtained from the analysis of 500 Raman spectra collected simultaneously over 1.5 hours. (a) Sample 2C3 (inhomogeneous); (b) Sample 5W7 (more uniform).

**FIG. 3** Map of fraction of monoclinic phase in the vicinity of the contact point of a MgO-PSZ quarter sphere produced in a compression test: (a) Full view of the face of the quarter sphere. The grid indicates the positions of the measured profiles. As shown in the magnified view, the resolution parallel to the sphere axis is the grid spacing (0.5 mm) and the resolution perpendicular to the sphere axis is one fifth of the grid spacing (55  $\mu\text{m}$ ); (b) Schematic of the double hemisphere compression test; (c) Contour map of monoclinic fraction near the contact point.

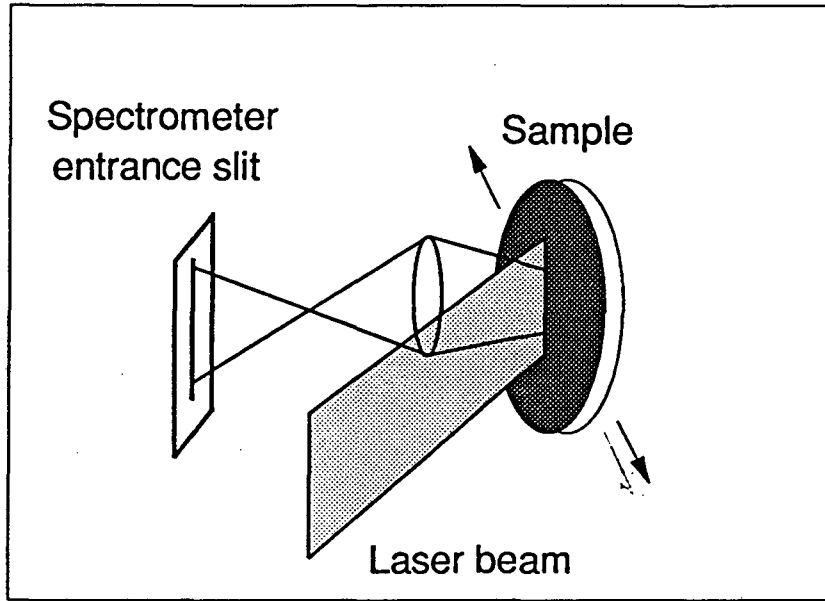


Fig. 1

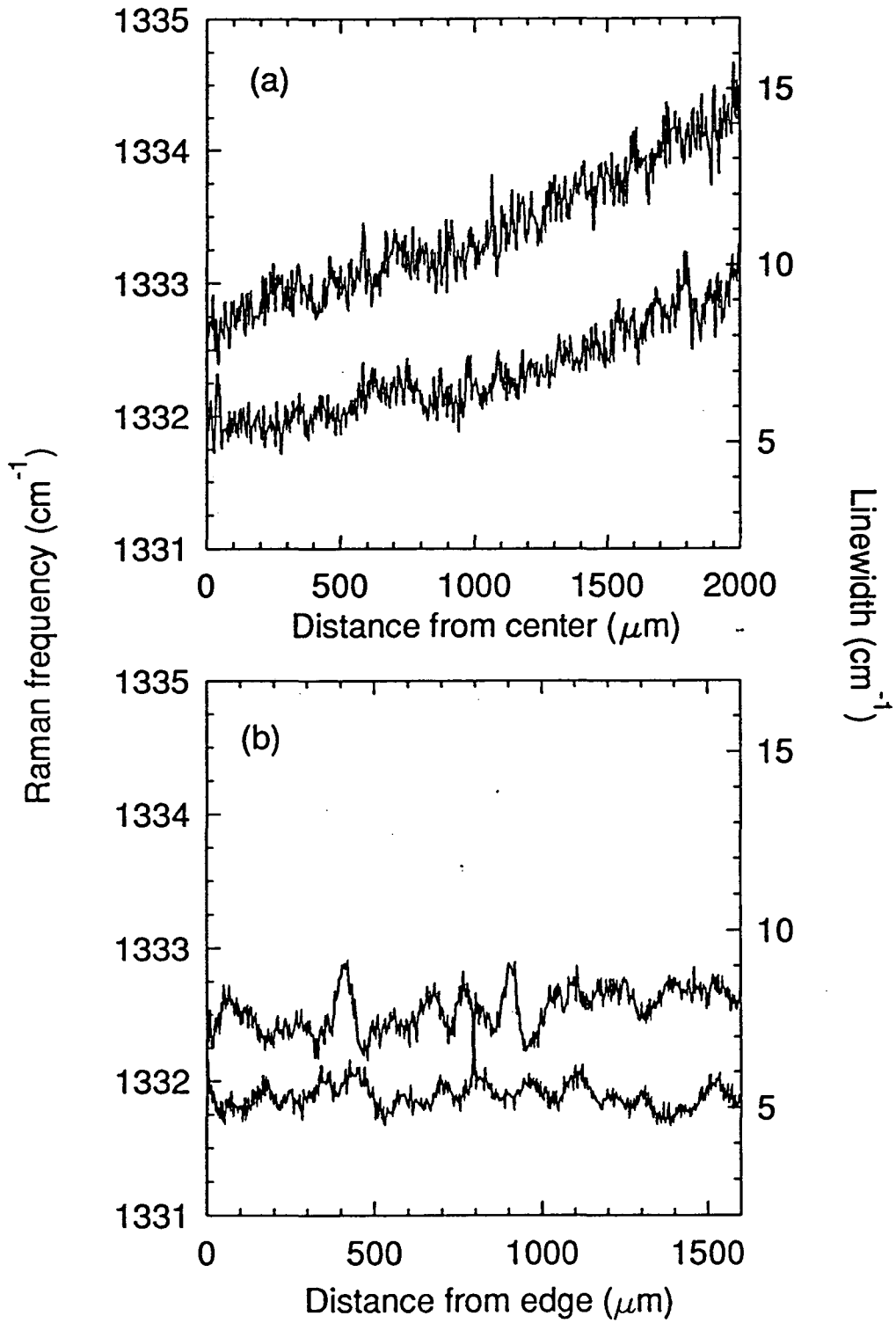


Fig. 2

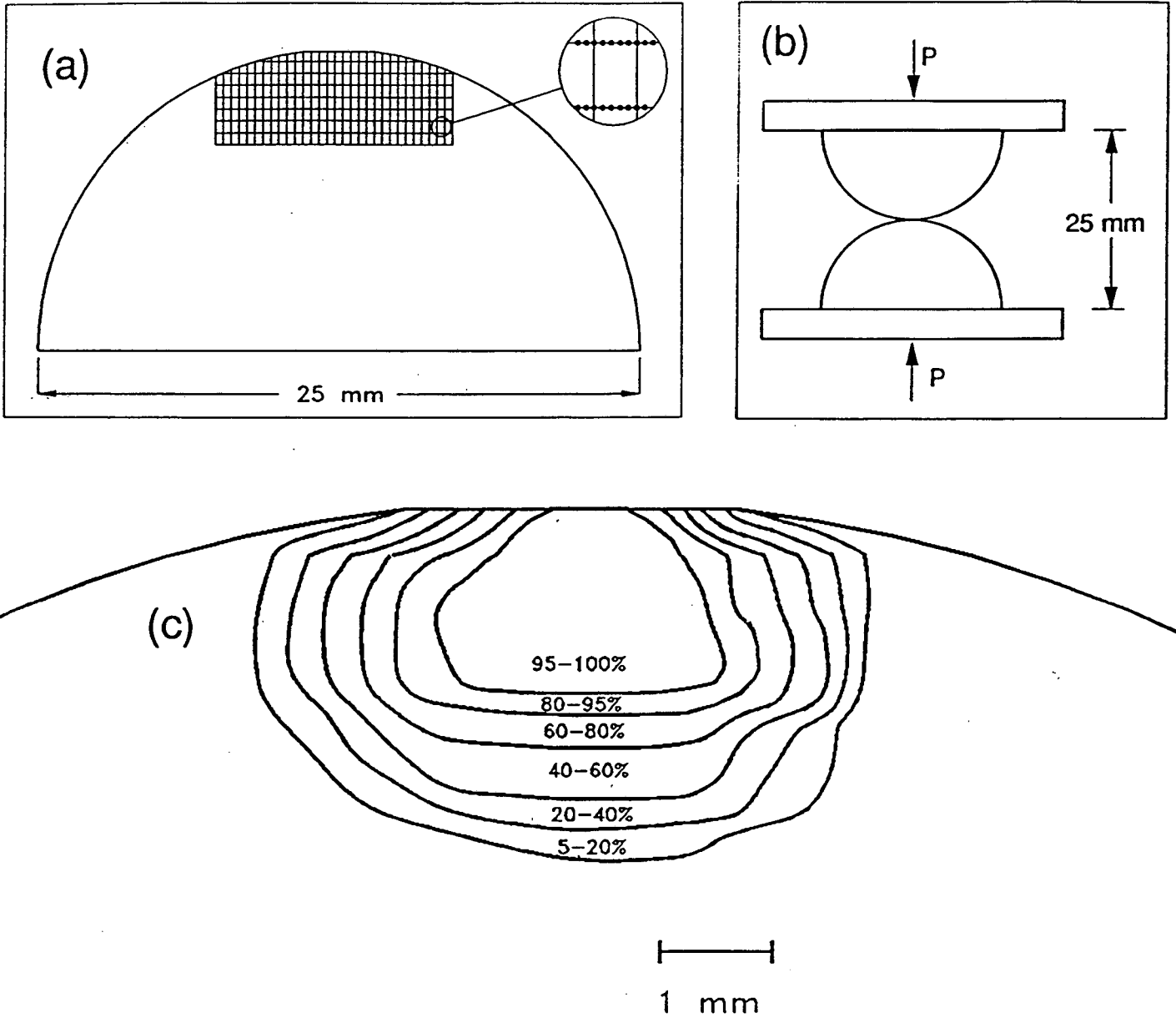


Fig. 3

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