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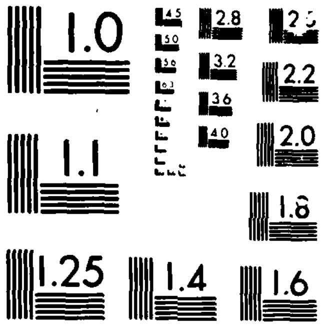
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AFOSR-TR- 86-0156

AD-A167 008

Final Report

# RAMAN SPECTROMETER WITH
# MICROPROBE CAPABILITY

Department of Defense (DOD) University Research
Instrumentation Program (FY1984/FY1985)

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This report describes the results of this equipment grant funded as a part of the Department of Defense (DOD) University Research Instrumentation Program. for fiscal years FY1934/FY1935. This grant funded the purchase of a Raman spectrometer with microprobe capability having resolution of 1.0 micron. This report describes the equipment selecting decision, the configuration of the instrument selected, and some experimental results. The experimental results include Raman spectra used in characterization of laser recrystallized silicon and ion implanted regions in semi-insulating GaAs.

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MATTHEW J. KERPER
Chief, Technical Information Division

## INTRODUCTION

This grant was funded as a part of the Department of Defense (DOD) University Research Instrumentation Program for fiscal years FY1984/FY1985. The funding in this grant was provided to allow purchase of a Raman spectrometer with microprobe capability. The microprobe capability allows Raman measurements to be performed on a localized area with a resolution of 1.0 micron.

One of the primary intended uses of this instrument is for the characterization of the crystallinity and the state of strain of laser annealed and laser recrystallized materials, especially polysilicon on amorphous substrates. The creation of large single crystal grains of unstrained, device quality silicon by laser annealing of polysilicon has many important device implications including improved signal processing by integrated optical waveguide detection, silicon CCD integration with InSb and HgCdTe infrared detectors, a silicon-on-insulator technology, and multilevel devices. The Raman microprobe can be used to characterize the effects of substrate temperature, beam power density and shape, beam scan speed and direction, deposition rate, substrate seeding, and polysilicon encapsulation schemes both near and away from grain boundaries. The frequency shift and the peak width of the Raman scattering from the triply degenerate zone center phonon in Si allow determination of the strain in the grains of laser recrystallized polysilicon. Reducing these strains will allow us to achieve large single grains of device quality.

A second intended use of the Raman spectrometer with microprobe is to characterize $Si_3N_4$ films and thermally nitrided layers of $SiO_2$ each

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formed on silicon substrates. As both of these layers are transparent to Argon-ion laser light used for Raman scattering, the Raman spectra obtained from samples having either of the above two layers on silicon substrates are dominated by structure associated with the silicon substrates. To overcome this, we plan to couple the Argon-ion laser light into $Si_3N_4$ and thermally nitrided layers which form planar optical waveguides and collect the light scattered from the waveguides for Raman analysis. We will form samples with layers of $SiO_2$ between the waveguiding layer and silicon substrate which are sufficiently thick so that the light is isolated from the silicon substrate. The scattered light will thus not have encountered silicon so that associated spectral characteristics will not be present, thereby improving sensitivity. The increased path length of light through the regions of interest should also significantly enhance sensitivity.

Another intended use which we plan to investigate is characterization of ion implanted regions in semi-insulating GaAs which have been either furnace annealed or rapid thermally annealed. Structural differences in samples annealed by the two different techniques may be apparent in Raman spectra.

In what follows we describe first our purchase process. The instrument actually purchased is then described. Preliminary Raman spectral data in several of the above areas is then presented.

## EQUIPMENT SELECTION

A Raman spectrometer with microprobe capability is available from only two companies, Spex Industries, Inc., Metuchen, N.J. and Instruments SA, Inc., also Metuchen, N.J. Both these companies have been suppliers of quality Raman spectrometers for some time, and both in the past few years have designed and implemented the addition of a microscope to their respective spectrometer systems. The monochromator in both of these instruments is of the Czerny Turner configuration, both use holographic gratings of 1800 grooves/mm, and both quote an ultimate resolution of 0.15 $cm^{-1}$. In part because the quoted specifications for each instruments were so similar, one of us (HEJ) spent one day at ISA and one day at Spex evaluating their respective instruments for use in our research. The evaluation included detailed discussions with technical personnel on our particular needs as well as with the instrument to obtain Raman data on several of our samples using both the usual sample chamber and the microscope capability. Based on these experiences, we concluded that the ISA instrument offered a superior microprobe facility, their monochrometer possessed better stray light rejection capability, and that their computer was somewhat more versatile. Accordingly, we selected the ISA instrument for purchase.

The ISA instrument with microprobe capability which was selected for purchase consists of several parts. Most importantly is the Czerny-Turner double monochrometer fitted with holographic master gratings with 1800 grooves/mm. The slits are horizontal and installed in a section outside of the main body of the monochrometer for superior stray light rejection. A Nachet microscope with 10x, 40x, and 80x objectives is optically interfaced with the double monochrometer in such a way that switching from the usual Raman mode of operation to the microprobe mode of operation may be done simply and without loss of alignment. The spatial resolution at highest magnification is 1 micron. A GaAs cooled photomultiplier and associated photon counting electronics provides the scattered light detection capability. The instrument is interfaced with a computer which is capable of not only controlling the instrument, allowing for very long scan accumulation times for instance, but also of performing data reduction tasks while the spectrometer is being actively controlled. The entire instrument is mounted on a vibration-free optical table with the argon-ion laser and Pellin-Broca prism assembly for removal of the laser plasma lines both mounted on a shelf attached to the underside of the table. A photograph of the instrument showing the microprobe end may be found in Fig. 1.

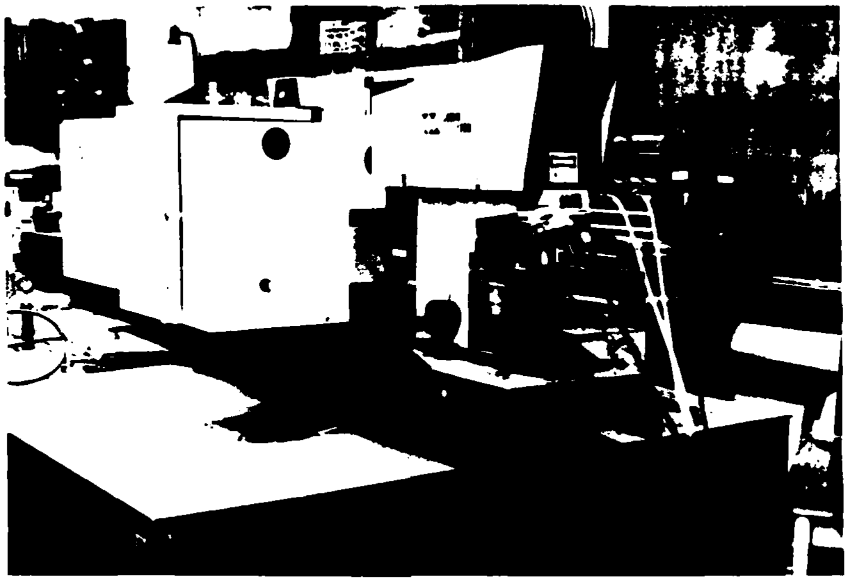

Fig. 1 Photograph of Raman spectrometer with microprobe mounted on vibration free table.

## PRELIMINARY RAMAN DATA

We present preliminary Raman data for three different research areas that were mentioned above: 1) Raman scattering from laser recrystallized silicon, 2) Raman scattering from ion-implanted GaAs, and 3) Raman scattering from thermally nitrided $SiO_2$ waveguides.

### Laser Recrystallized Polysilicon

Raman scattering from laser recrystallized polysilicon probes the local state of strain in the silicon. By comparing the Raman shift of the longitudinal optic phonon in bulk silicon to that observed in the laser recrystallized polysilicon, the magnitude of that strain may be measured in a contactless manner. The use of the microprobe allows us to quantify this strain with 1 micron spatial resolution and thus to understand the spatial variation of strain that may lead to grain boundary formation or simply to a different amount of strain as laser power densities are varied. In Fig. 2 we display a portion of the Raman

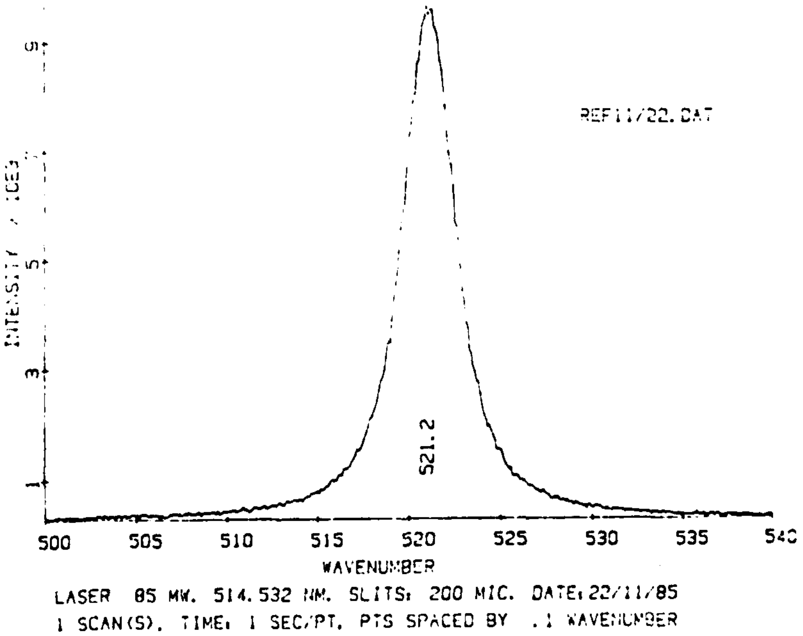

Fig. 2 Raman scattering from a silicon wafer.
See text discussion.

521.2 $cm^{-1}$, in good agreement with values reported in the literature, and the linewidth is quite narrow. Figure 3, in contrast, is a typical spectrum of polysilicon deposited by a CVD process. Note the broadened peak at about 520 $cm^{-1}$ and the shoulder at about 495 $cm^{-1}$, both features associated with the degree of disorder in the sample. In Fig. 4 is a Raman spectrum of a laser recrystallized sample where the polysilicon was deposited on a 1 micron layer of thermally grown $SiO_2$ and capped with 60 Angstroms of $Si_3N_4$. Note that although the linewidth is quite narrow, the peak has shifted by 3 $cm^{-1}$ compared to bulk silicon, indicating that the single crystal silicon we have fabricated on the $SiO_2$ substrate is strained. In contrast, in Fig. 5a we display Raman data from a sample with stripe anti-reflection coatings for the capping

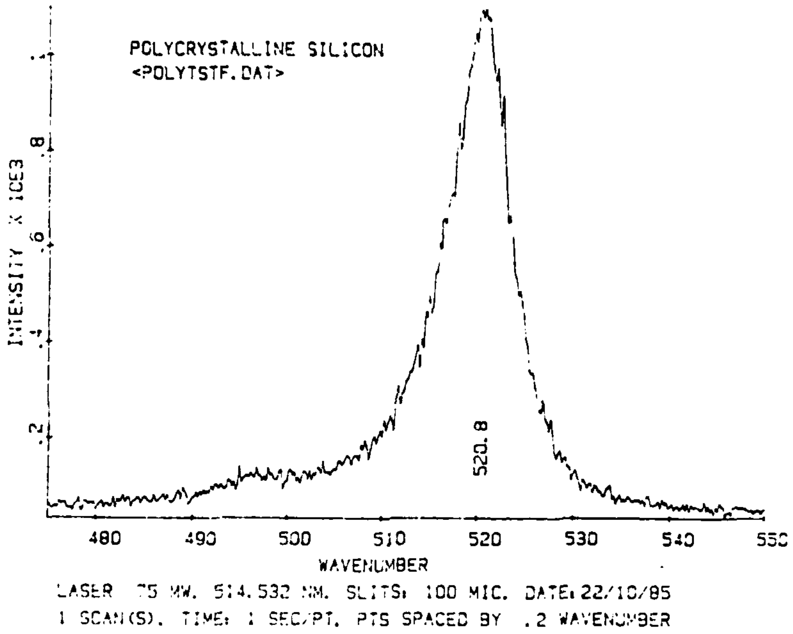

Fig. 3 Raman scattering from CVD deposited polysilicon.

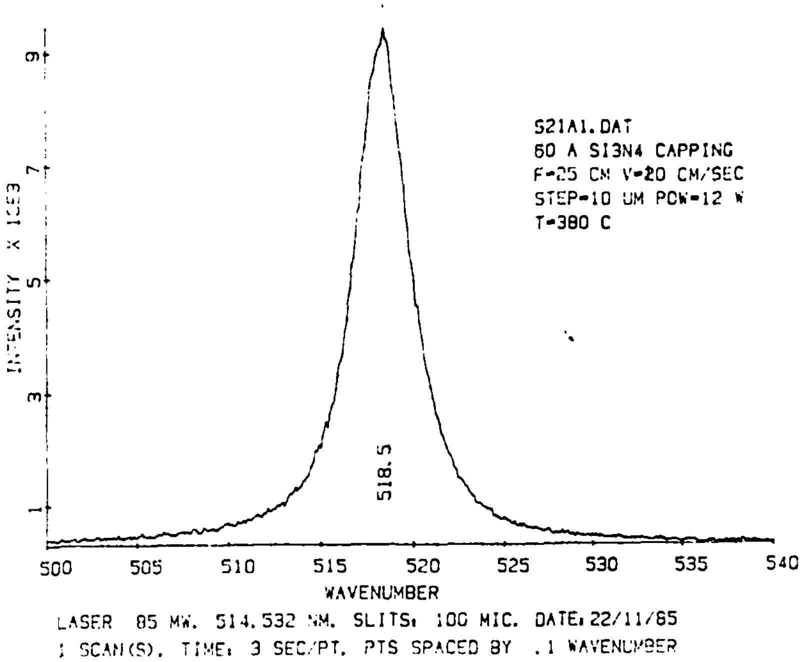

Fig. 4 Raman scattering from laser recrystallized silicon.

layer where, although the peak position of the Raman line is similar to Fig.4, the linewidth is clearly wider even after noting the expanded horizontal scale. We do not fully understand this increase in width at this time. What is clear from an examination of Fig. 5b, the Raman data for a point 1 micron further distant from a grain boundary than the previous spectrum, is that the grain boundary provides relief from the strains induced in this structure by the laser recrystallization process. In other words, the strain changes dramatically as one moves away from the grain boundary (i.e. the Raman shift decreases from 518.2 $cm^{-1}$ to 516.8 $cm^{-1}$ over only one micron). We have found that the strain then becomes constant until another grain boundary is approached. spectrum of bulk silicon. The Raman shift of the LO peak is found to be

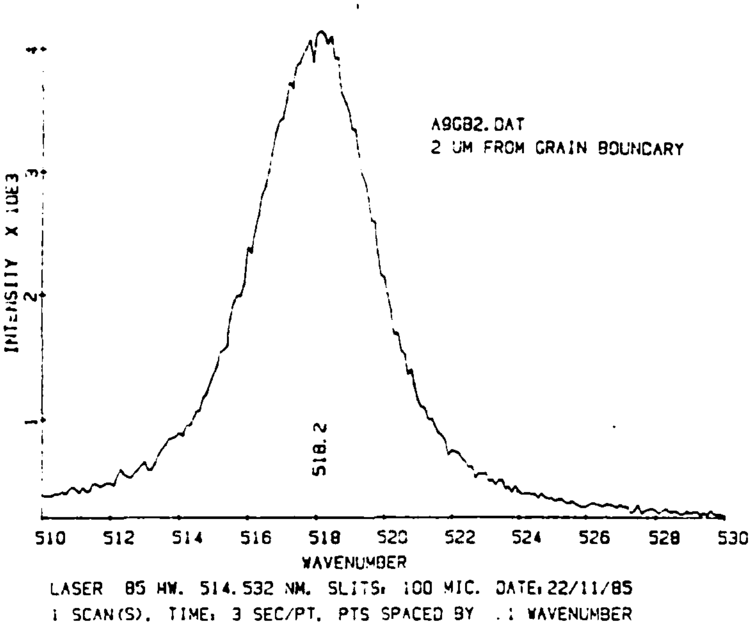

Fig. 5a Raman scattering from laser recrystallized silicon 2 microns from a grain boundary.

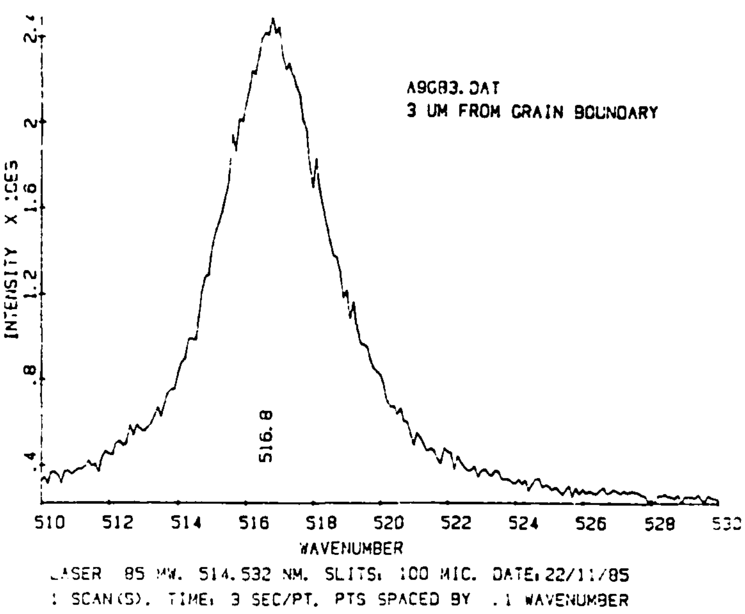

Fig. 5b Raman scattering from laser recrystallized silicon 3 microns from a grain boundary.

Efforts to understand these phenomena both as a function of laser recrystallization parameters and of variations in the polysilicon structures and to relate these observed changes to electrical characterizations important for device applications have just begun.

Gallium Arsenide

We mention briefly two other areas we are pursuing. Raman scattering can also be used as a contactless non-destructive probe of GaAs and $Ga_{1-x}Al_xAs$ to probe both the space-charge layer at surfaces and for determining the free carrier concentration. In Fig. 6 we present a preliminary Raman spectrum of GaAs. This sample was ion implanted with Si to a concentration of $2 \times 10^{17}$ $cm^{-3}$. Following ion implantation a rapid thermal annealing process was carried out to activate the implanted species. We see a strong Raman peak at 293 $cm^{-1}$ due to scattering from the LO phonon. If, however, a high enough concentration

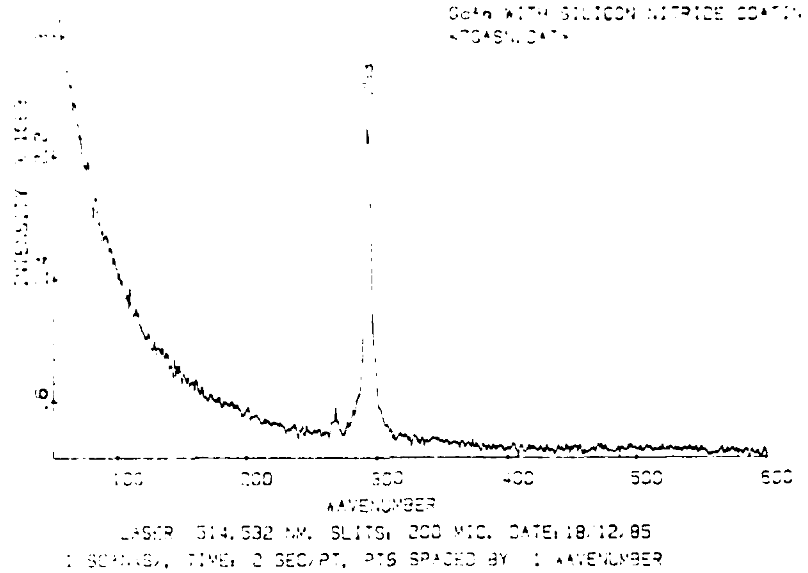

Fig. 6 Raman scattering from ion implanted GaAs.

of free carriers is present, then one expects not only the LO phonon but also coupled phonon-plasmon modes. These modes would be split away from the observed 293 $cm^{-1}$ peak for free carrier concentrations in excess of approximately 2 x $10^{17}$ $cm^{-3}$, about what is measured by electrical techniques. Thus in the present sample no coupled modes are seen and the free carrier concentration cannot be measured with Raman scattering. Rapid thermal annealing experiments on samples with higher free carrier concentrations as well as experiments on $Ga_{1-x}Al_xAs$ are planned.

## Thermally Nitrided Optical Waveguides

The non-destructive characterization of low loss optical waveguides is another area we are presently pursuing with the Raman spectrometer. In a preliminary experiment we have studied, using Raman scattering, very low loss optical waveguides formed by thermal nitridation of $SiO_2$ which had been formed by thermal oxidation of the bulk silicon substrate. In Fig. 7 we display data taken with the laser impinging perpendicular to the waveguide surface. The complex structure observed can be understood by considering second order Raman scattering of the underlying silicon substrate. Clearly we need to place the sample in the waveguiding configuration and observe the Raman scattering induced by the waveguided light. Such an experiment is in the final planning stages.

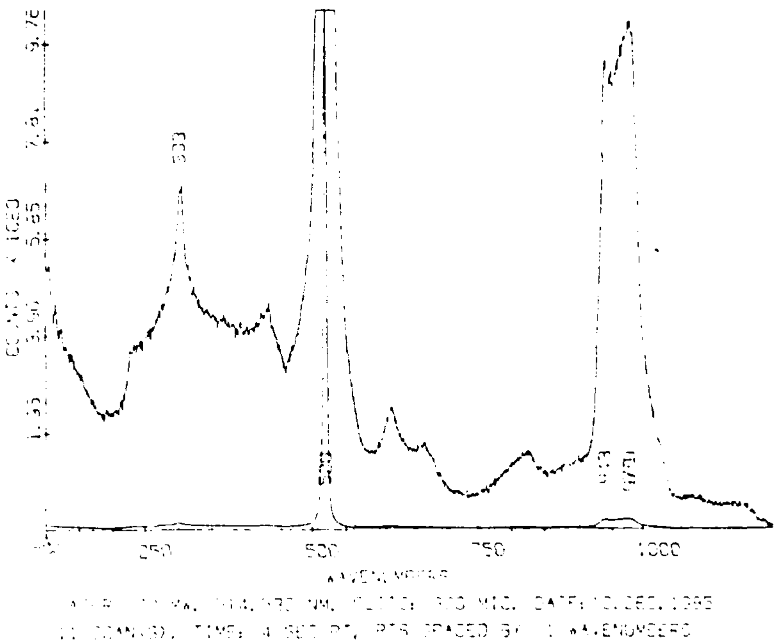

Fig. 7 Raman scattering from a thermally nitrided $SiO_2$ layer on a silicon substrate.

## SUMMARY

Following a careful evaluation and selection process, we have purchased and installed a Raman spectrometer with microprobe capability. In the first several months of operation we have performed a number of preliminary experiments on research problems involving laser recrystallized silicon, rapid thermally annealed ion-implanted GaAs, and very low loss thermally nitrided $SiO_2$ optical waveguides. All of these Raman scattering experiments show promise in advancing our present understanding of these problems.

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