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Control system of the Raman spectrograph

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Annotation – Universal apparatus for measuring Raman spectrography (RS) on surface of solid state samples was designed and realized. It enables to obtain Raman spectrum from the measured semiconductor sample excited by powerful Ar-ion or HeNe lasers, alternatively. The PC controlled equipment consists of a composite optical setup, lasers, optical monochromator, very sensitive CCD camera, micromanipulators, and electric circuits serving to extract relevant signal from the noisy background.

I. INTRODUCTION

Raman spectra of semiconductors are useful in characterising the bulk (excitation with lower-band-gap laser lines) and the surface region (excitation with higher-band-gap laser lines). From the phonon and free carrier excitation spectra, information about the lattice perfection, carrier concentration and mobility are obtained. The bonding properties which produce infrared and Raman-active vibration bands provide a useful fingerprinting technique for determining the presence or absence of different impurities. Metal nanoparticles placed on the surface of semiconductors can cause enhancement of Raman spectra by the effect called surface-enhanced Raman scattering – SERC. It can be used to study nanolayers of metal nanoparticles or to study organic molecules bound to nanoparticles.

II. PRINCIPLE OF THE RAMAN SPECTROSCOPY

The principle of the Raman spectroscopy is shown in Fig.1

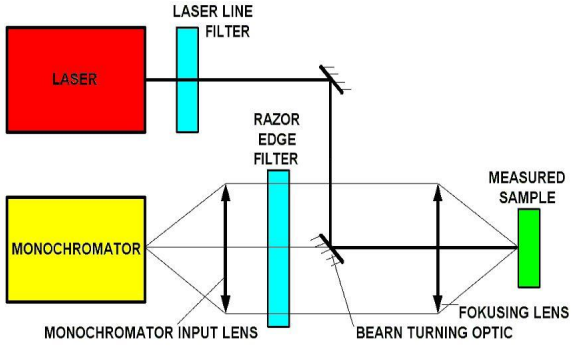

Fig.1, The principle of the Raman spectroscopy

The laser beam is filtered by the interference filter (Laser Line Filter) and with the help of small Bearn Turning Optic mirror directed to the optical axis of the measuring apparatus. The beam is further focused on the measured semiconductor sample using Focusing Lens objective. Interaction with the sample gives rise to emitted light whose wavelength is modulated by excited surface particles of the sample. One can evoke an analogy with radio engineering, where the HF carrier frequency is modulated by the LF signal. The emitted light is collimated into a parallel optical beam in backward direction, to the monochromator. The laser light is filtered out by the Razor edge Rayleigh interference filter and subsequently, using Monochromator Input Lens, concentrated into the input slit of the monochromator. In the site of the output slit, a CCD camera is located which is capable, without requiring rotation of the monochromator optical grid, to cover the totality of optical spectrum. One of the major advantages of dispersive Raman is that it offers the possibility to select the optimal laser excitation wavelength to permit the recording of the best Raman information. For example, wavelength can be selected to offer the best resonance with the sample under investigation. One might also need tune wavelength to avoid fluorescence and thermal emission backgrounds.

III. SETUP OF THE OPTICAL SYSTEM OF THE RAMAN SPECTROGRAPH

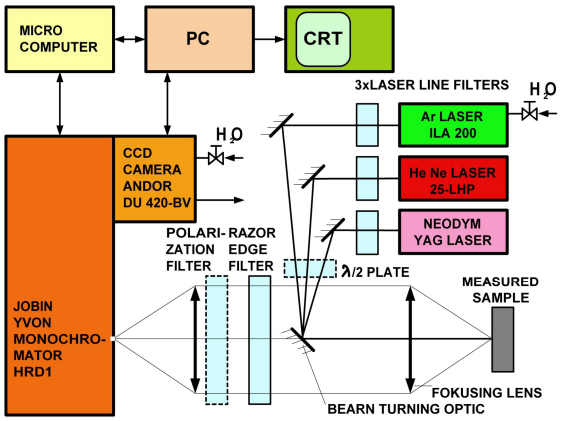

Fig.2, Setup of the optical system of the Raman spectrograph

Arrangement of the optical system of the Raman spectrograph is shown in Fig. 2.

Either of two installed lasers can be used alternatively, as source of the measured sample illumination. We use the argon laser LA200, in which both the glass laser tube and the high voltage source are water-cooled, and the Melles Griot He-Ne laser 25-LHP-928-230 [1]. Harmonic frequencies of these lasers are removed using two laser line filters whose transparency spectra are shown in Figs. 3 and 4. As a result, beyond the filters there is just a single narrow spectral line of the laser.

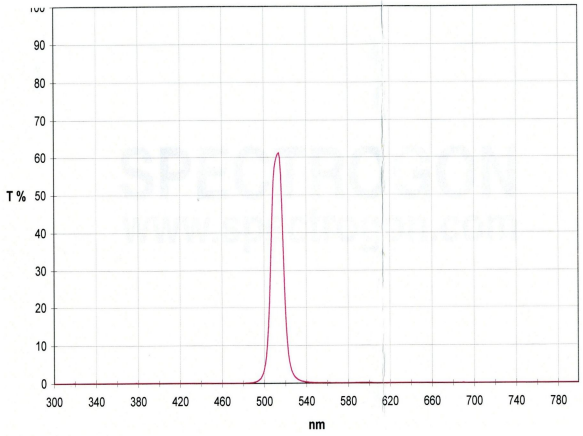

Fig.3, Transmission spectral curve of laser-line filter for Ar-ion laser

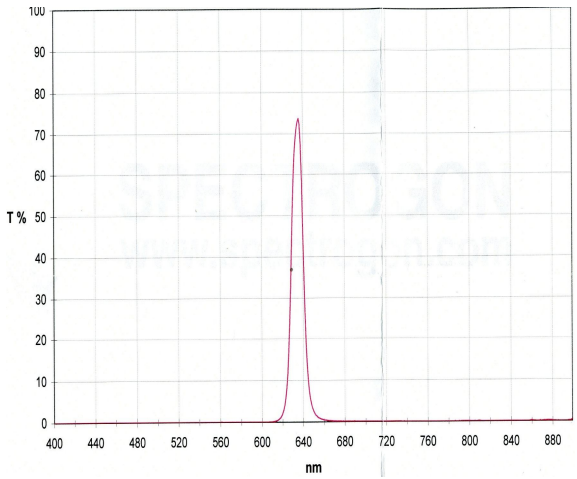

Fig.4, Transmission spectral curve of laser-line filter for He-Ne laser

Following reflection on mirrors, these beams are brought to a small bean turning optic mirror which directs the beam to the optical setup's axis. The focusing lens concentrates the optical beam on a very small area of the measured sample's surface. The light generated by Raman scattering from the surface is by the focusing lens collimated into a parallel optical beam. The relevant part of the optical spectrum is narrowly and sharply selected with the help of Razor edge filters. Their transmission spectra for Ar and HeNe lasers are in Figs. 5 and 6. The performance of these Semrock (USA) products [2], measured by the steepness and selectivity (just several nm from the laser spectral line) is amazingly excellent.

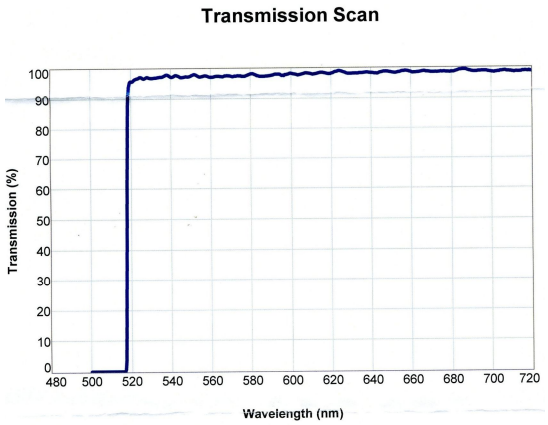

Fig.5 Transmission Scan for Razor edge filter for Ar-ion laser

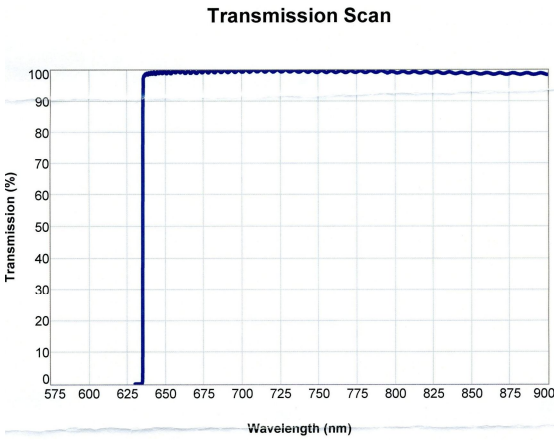

Fig.6 Transmission Scan for Razor edge filter for HeNer laser

Intensity of the Raman spectrum in dependence on polarization plane of the light is measured by the rotation polarization filter and a λ/2 plate.

We use double-grid Jobin-Yvon HRD1 monochromator [3] with a CCD camera located at the output slit. Its schema is in Fig. 7.

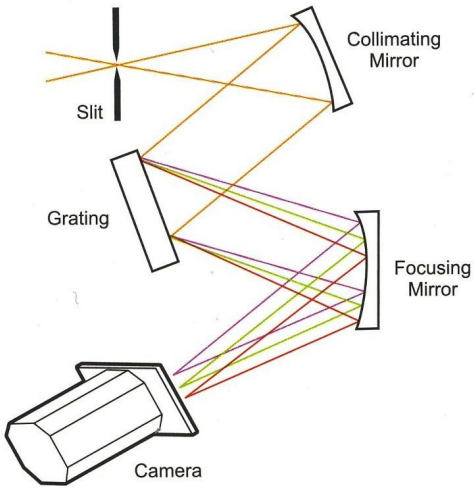

Fig.7, Illustration of the principle of Czerny-Turner Spectrograph

A spectrograph typically contains two types of optics. The first forms an image of the source; the second disperses the light or makes an angular deflection of the light as a function of the wavelength. Together make an instrument which forms multiple images of the source, one for each of the separate resolved wavelengths. In the Czerny-Turner spectrograph the imaging optics use a pair of concave mirrors and the dispersive element is a plane grating. The second mirror gathers the light from the grating and directs the multiple images of the input slit onto the detector.

The monochromator used by us is a double-grid variety which employs series arrangement of two Czerny-Turner units. The second grid refines the interference pattern created by the first grid.

The crucial element of the whole apparatus is a highly sensitive CCD camera Andor iDus [4]. Its core constitutes a 1024 × 256 pixel CCD circuit placed in vacuum. The camera is thermoelectrically cooled by Peltier elements. With additional water cooling, temperature of -100°C can be attained on the CCD detecting circuit, thereby drastically reducing thermal noise of the detector. Camera's interior is evacuated to avoid water condensation on the CCD element.

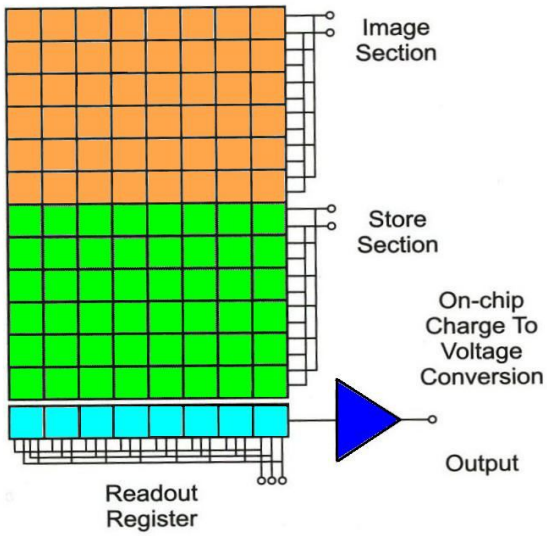

Fig.8, Typical CCD structure

On Fig. 8 is the typical CCD structure. Silicon diode photo sensors (pixels) are coupled to an Image Section area, which is copied to a charge storage region that is, in turn, connected to an amplifier that reads out the quantity of accumulated charge. Incident photons generate electronic charges, which are stored in the charge storage region.

On Fig. 9 is the structure of the iDus Andor CCD camera.

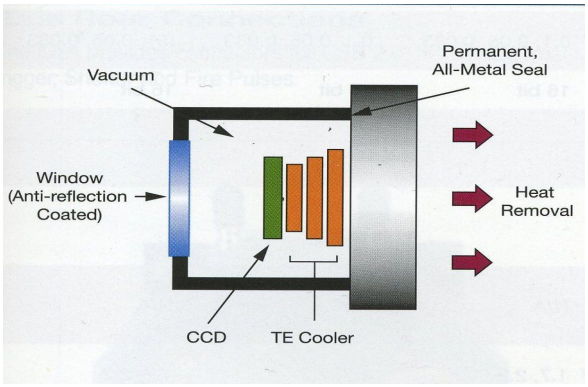

Fig.9, Structure of the iDus Andor CCD camera

The equipment has been used for characterization the metal nanoparticle layers on semiconductors

prepared by electrophoretic deposition [5]. It has been shown that, with the deposition of silver nanoparticles, Raman spectrum of InP has been enhanced by the factor of 50, due to the effect of surface enhanced Raman scattering (SERC) [6]. Another example of Raman spectrum measured with the described equipment is shown in Fig. 10 on the sample of PbI_2 crystals prepared by M. Matuchova et al. [7]. Two Raman lines labelled A_{1g}, correspond to the Raman-active breathing mode and the shear deformation mode, respectively. A third line, LO, is unresolved at room temperature and consists of two lines. The one at 113 cm^{-1} is attributed to the longitudinal polar mode A_{2u} and the other one at 106 cm^{-1} to the longitudinal polar mode E_{1v} [8]. As this Raman spectrum is highly sensitive to crystal defects, it can be useful for estimating the sample quality.

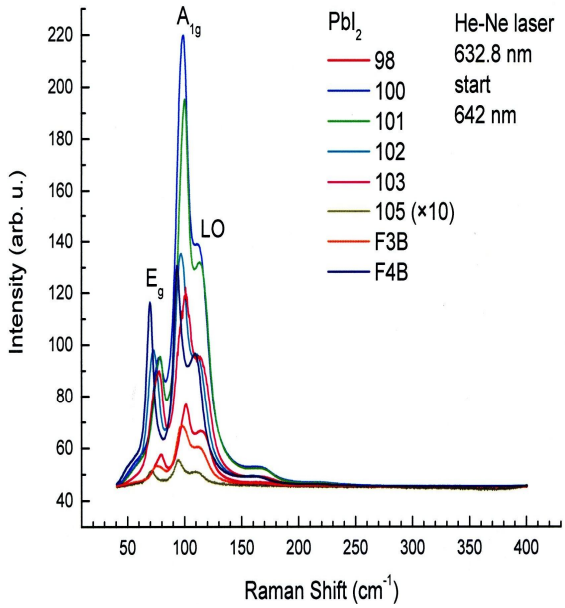

Fig. 10, Typical Raman spectrum of PbI_2 crystal. The sample was excited at room temperature by He-Ne laser line at 632.8 nm.

IV. CONCLUSIONS

Raman spectrograph of high sensitivity for measurements of solid state samples at room temperature with the excitation by Ar-ion and He-Ne lasers has been designed and realized. It has been used for characterization of semiconductor crystals and structures of semiconductors with nanolayers of metal nanoparticles, studying the effect of SERS. In the case of PbI_2 samples the Raman spectrum can be useful for monitoring their crystal quality. Extension of the Raman spectrograph for the measurement at low temperatures, down to liquid helium temperature is in progress, as well as the extension for the measurement with the excitation by Nd: YAG laser.

On the Fig.11 is the electro-optical setup of the described measuring system.

Fig. 11, Electro-optical setup of the described measuring system

V. ACKNOWLEDGMENTS

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http://www.cvimellesgriot.com/Products/High-Power-Helium-Neon-Laser-Systems.aspx

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