UV lasers in Raman spectroscopy

A solid-state 320 nm laser enables the replacement of HeCd gas lasers for the analysis of ferroelectric perovskite thin films and heterostructures.

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Cobolt Zydeco™ 320 nm laser with laser head (115 × 55 × 45 mm³) and controller unit

All images: HÜBNER Photonics – Cobolt

Laser technology has evolved significantly over the years, driven not only by advances in engineering and optics but also by increasing environmental and regulatory pressures. In particular, the EU has initiated the phased restriction of cadmium. As a result, it is becoming increasingly interesting to look for safer laser alternatives to helium-cadmium lasers. We demonstrate how new diode-pumped solid-state lasers can serve as a very attractive alternative.

Ultraviolet Raman spectroscopy has emerged as a powerful technique with a wide range of applications. In chemistry, biology, and pharmacy, UV excitation offers several advantages, including enhanced sensitivity and signal-to-noise ratio of the Raman spectra, resonant excitation, and the effective suppression of fluorescence background. The fluorescence response of complex organic compounds and biological samples can be reduced by using a longer wavelength and is often eliminated by using near infrared excitation, such as 1064 nm. Another option is to excite Raman spectra at wavelengths below the fluorescence window using UV excitation. In addition, UV excitation can induce a pronounced resonance enhancement of the Raman signal – by up to 2 – 4 orders of magnitude – in certain samples. Moreover, owing to its shorter wavelength compared to visible or infrared radiation, UV light enables improved spatial resolution in micro-Raman spectroscopy, facilitating detailed mapping of molecular structures and Raman imaging.

Commonly used in UV Raman spectroscopy analysis are helium-cadmium lasers (HeCd). Those gas lasers emit in the visible and ultraviolet regions, most commonly at wavelengths of 442 nm (blue) and 325 nm (UV). HeCd lasers are valued for their ability to deliver stable, continuous-wave light with a narrow linewidth, high spectral purity, and excellent beam quality with a TEM_{00} mode, making them ideal for precision applications such as Raman and fluorescence spectroscopy, holography, and photolithography. Their low intensity noise, long coherence length, and stable linear polarization further enhance their suitability for sensitive optical measurements. These features have made HeCd lasers a standard in scientific and industrial fields requiring high-resolution optical excitation.

However, HeCd lasers rely on cadmium, a highly toxic and environmentally hazardous material, which poses significant regulatory, handling, and disposal challenges. Moreover, HeCd laser systems are bulky and inefficient, require frequent maintenance, and suffer from limited operational lifetimes. Consequently, there is growing interest in the development of alternative light sources to replace HeCd lasers. One promising alternative is a diode-pumped, frequency-converted solid-state laser at 320 nm. Such lasers represent a safer, more efficient, more compact, and more sustainable alternative to HeCd lasers. We thus focus on the advantages of UV excitation in Raman spectroscopy for characterization of nanoscale inorganic materials, in particular, wide-bandgap semiconductors and dielectrics, while demonstrating how the use of a compact diode pumped solid state (DPSS) 320 nm laser compares to the use of a HeCd laser at 325 nm.

Raman analysis of thin films

Complex oxides are a vast class of materials that have a wide variety of functional properties. Among these functionalities, ferroelectricity has been intensively studied over the past few decades. Ferroelectrics are a class of materials that exhibit a spontaneous electric polarization arising from the ordered arrangement of electric dipoles, which can be switched between crystallographically defined directions by the application of an external electric field. Ferroelectric materials have been investigated for various device applications such as non-volatile memory, piezoelectric micro- and nanoelectromechanical systems, tunable microwave devices, integrated optics and photovoltaics applications. Advances in epitaxial oxide thin-film deposition have rapidly driven the science and technology of ferroelectrics toward nanoscale thin films and multilayer structures. Nanoscale ferroelectrics are of considerable interest from a fundamental physics perspective, as the reduction of structural dimensions gives rise to novel phenomena and properties that differ markedly from those of bulk ferroelectrics.

Central to understanding the fundamental properties of ferroelectrics is the dynamics of the crystal lattice, which is intimately linked to the phenomenon of ferroelectricity. Lattice dynamics in bulk perovskite oxide ferroelectrics have been investigated for several decades using neutron scattering, far infrared spectroscopy, and Raman scattering. Raman spectroscopy is one of the most powerful analytical techniques for studying lattice vibrations and other elementary excitations in solids providing important information about structure, composition, strain, defects, and phase transitions. Studying lattice dynamics in ferroelectric films and heterostructures thinner than ~100 nm has been challenging.

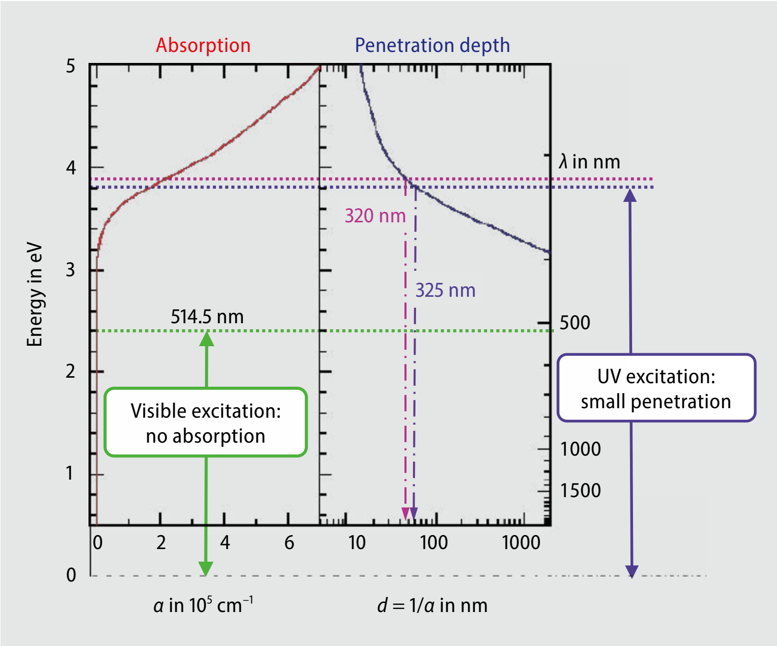

Fig. 1 The graph shows the absorption coefficient a and the penetration depth d of light in $BaTiO_3$ compared to the energies of visible (514.5 nm) and UV (325 and 320 nm) photons (absorption data from Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology, New Series, Group III, 36(A1), Springer, Berlin, 2001).

A major challenge in applying conventional Raman spectroscopy to ferroelectric thin films and other wide-bandgap materials using visible or near-infrared excitation is that the photon energy in the visible range is much smaller than the material bandgap. Consequently, light absorption is extremely weak and the penetration depth is large, allowing the incident light to pass through the thin film and into the much thicker substrate. Owing to its substantially larger scattering volume, the substrate therefore generates dominant and often overwhelming contributions to the Raman spectra. For UV excitation, the photon energy is above the bandgap of ferroelectric oxides such as $SrTiO_3$ or $BaTiO_3$ which leads to a much stronger absorption (**Fig. 1**).

Using UV excitation enables the investigation of nanometer-thin films and heterostructures owing to the greatly reduced penetration depth, thereby suppressing the overwhelming substrate contributions that dominate Raman spectra obtained with visible excitation. [1]. Moreover, many oxide materials such as $BaTiO_3$, $SrTiO_3$, and ZnO possess bandgaps in the range of 3.0 – 3.5 eV, making UV excitation particularly advantageous for the characterization of high-temperature phase transitions in ferroelectric materials. A difficulty in measuring Raman spectra of materials at high temperatures

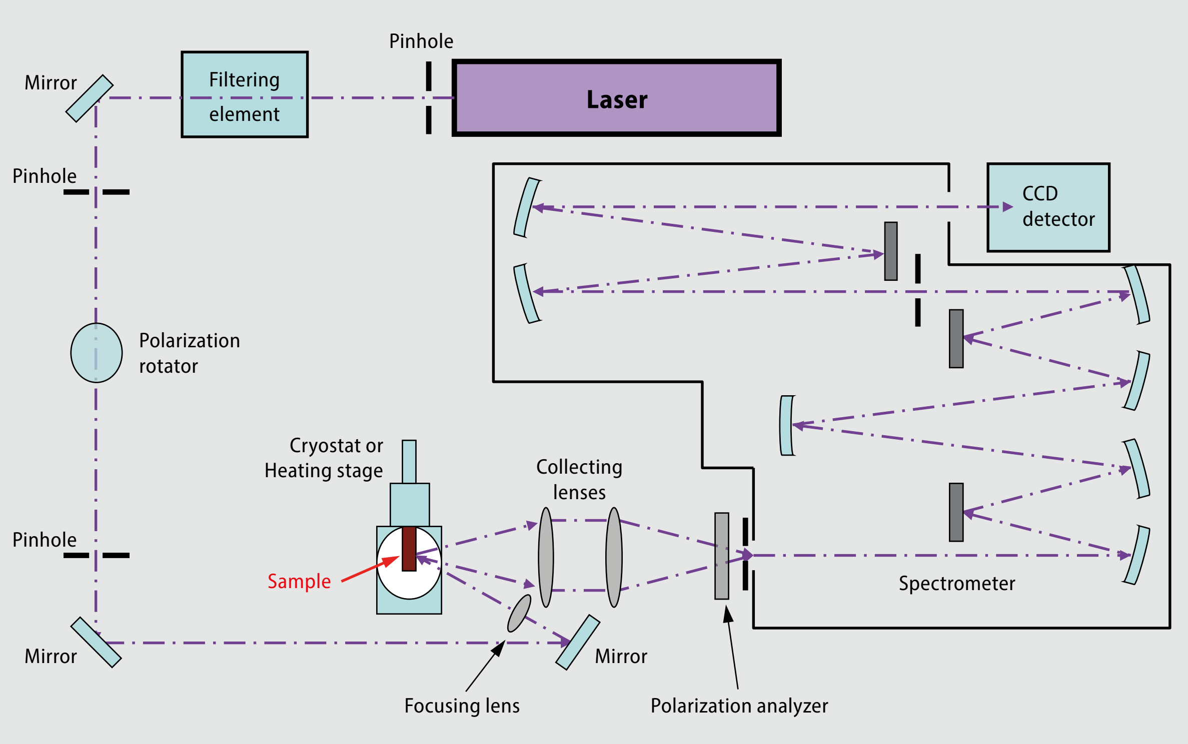

Fig. 2 The beam path in this experimental setup uses dielectric mirrors with low optical loss and high reflectivity, as well as quartz glass lenses with anti-reflective coating to minimize optical losses.

using visible excitation is caused by continuous background due to thermal emission, which can be rather intense compared to weak and broadened Raman features. UV excitation shifts Raman spectra to a much shorter wavelength range, far away from the peak intensity of thermal radiation.

Comparison of solid-state 320 nm with HeCd 325 nm

Raman studies of ferroelectric oxides and many other dielectric and semiconductor materials often involve measurements of phonon lines at Raman shifts below 300 cm^{-1}, not to mention the soft phonon modes, which are usually observed below 100 cm^{-1} (as low as 10 cm^{-1}). Therefore, effective Rayleigh scattering filtering and stray light reduction are required. In the UV range this is usually achieved by triple monochromators using subtractive double monochromators as a filter for stray light reduction. In this study, the spectra were recorded using a Horiba Jobin Yvon T64000 triple spectrometer equipped with a liquid-nitrogen-cooled multichannel charge-coupled device (CCD) detector optimized for the UV spectral range.

UV excitation near the bandgap can also result in a resonance enhancement of the Raman signals. When combined with the intensity increase arising from the ω^4 dependence of the Raman scattering cross section, this provides UV excitation with a further advantage over visible excitation. For bulk dielectric crystals and ceramics, the scattering volume V can be orders of magnitude larger under non-absorbing visible excitation, resulting in a higher overall scattering intensity – unless the laser energy is precisely tuned to an electronic or excitonic resonance. In nanoscale films, however, V is typically governed by the film thickness rather than the optical penetration depth. Consequently, the resonant enhancement and the ω^4 dependence of the Raman scattering cross section lead to a substantially stronger UV Raman signal from thin films of ferroelectric oxides and other wide-bandgap materials compared with visible excitation.

With this experimental setup (**Fig. 2**), spectra of various ferroelectric oxide thin film heterostructures were measured using a 325 nm HeCd laser as excitation source, then with the same experimental setup a Cobolt Zydeco™ 320 nm laser was introduced to generate comparative Raman spectra with a solid-state laser. The Cobolt Zydeco™ 320 nm laser provides single-frequency emission at 320 nm with up to 20 mW output power in a TEM_{00} beam. The emission has a linewidth of < 500 kHz, a very high spectral purity with SMSR of > 60 dB at < 500 pm from the main peak (< 50 cm^{-1}), a wavelength stability of < 1 pm and a guaranteed lifetime of twelve months with unlimited hours of operation.

Figure 3 shows comparative Raman spectra of a ferroelectric thin film measured with excitation wavelengths of 325 and 320 nm, using a 200 nm-thick $Ba_{0.45}Sr_{0.55}TiO_3$ film grown by molecular beam epitaxy on a (110)-oriented $DyScO_3$ substrate as an example. As can be seen from **Fig. 3**, the spectra measured at Raman shifts as low as 20 cm^{-1} from the laser line are essentially identical, demonstrating that both lasers are suitable for acquiring high-quality Raman data from these materials. Nevertheless, the 320 nm laser offers several advantages over the HeCd laser. The Cobolt Zydeco™ 320 nm laser is much more compact, with the laser head measuring only 115 × 55 × 45 mm^3 versus the 1420 × 146 × 197 mm^3 HeCd laser of comparable emission power. The Cobolt power supply is also much more compact, and the system power consumption is less than 65 W, compared to ~700 W for a HeCd laser. Compactness is particularly beneficial in setups with space limitations, e.g. micro-Raman spectrometers utilizing interchangeable lasers. In addition, solid-state lasers do not require interference filters that are needed when carrying out Raman measurements with gas lasers to filter out plasma lines.

Conclusions

Helium-cadmium (HeCd) lasers have long been employed in ultraviolet (UV) Raman spectroscopy owing to their stable single-frequency emission and excellent beam quality. However, their reliance on cadmium – a highly toxic material – together with their bulky design, low efficiency, and high maintenance needs, has rendered them increasingly incompatible with modern environmental and regulatory standards. UV Raman spectroscopy itself offers major advantages in chemistry, biology, and materials science by reducing fluorescence background, enhancing Raman signals, and improving spatial resolution, such as for nanoscale ferroelectric thin films. Here it is shown that diode-pumped solid-state (DPSS) UV lasers, such as Cobolt Zydeco™ 320 nm laser, can replace the 325 nm HeCd laser line, delivering high-quality Raman spectra while offering significant benefits in compactness, efficiency, stability, and sustainability.

References

[1] *D. A. Tenne* et al., Science **313**, 1614 (2006)

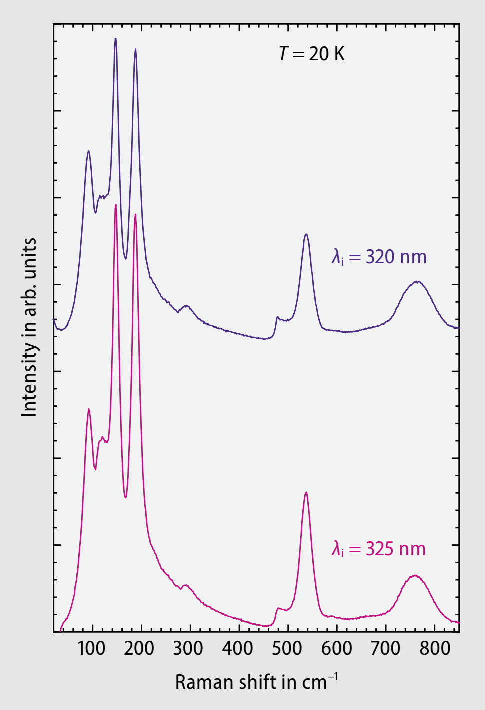

Fig. 3 Raman spectra of an epitaxial 200 nm-thick $Ba_{0.45}Sr_{0.55}TiO_3$ film on a $DyScO_3$ substrate, excited at 325 nm (20 mW, HeCd laser) and with 320 nm (20 mW, Cobolt Zydeco™).

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