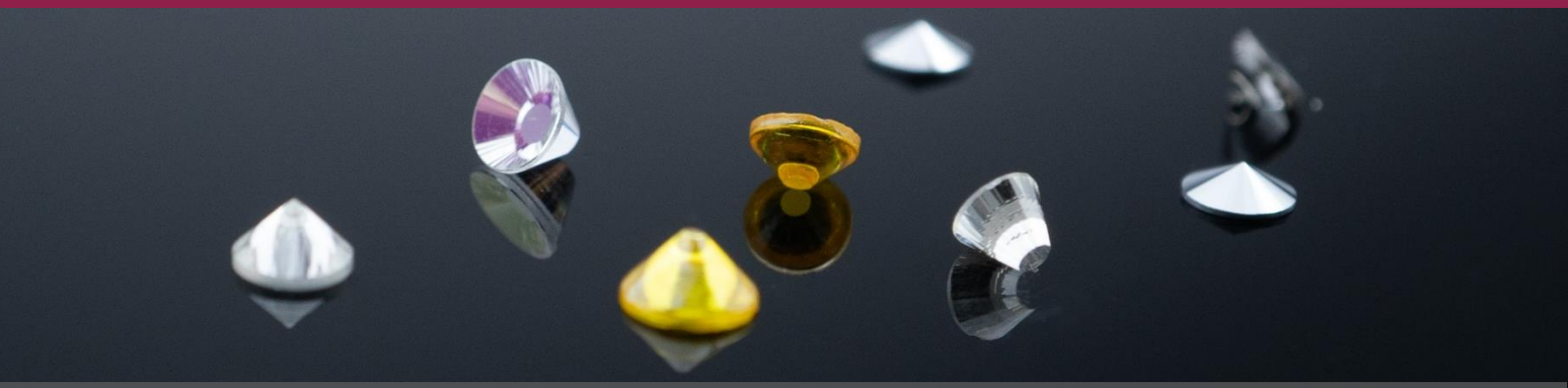

ATR Crystal Choice for Fiber-based Process Spectroscopy

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Introduction

Attenuated Total Reflectance (ATR) fiber probes are used for research and industrial applications including real-time process monitoring in the chemical, petrochemical, nuclear, biopharmaceutical and food industries. Selection of the appropriate probe, including the ATR crystal, is critical for effective and reliable measurements. This Technical Note gives a short overview of the different ATR crystals available at art photonics.

Fiber based ATR spectroscopy

ATR spectroscopy is a widely used method for analyzing various types of liquid and pasty mixtures with minimal preparation. It works by directing an optical beam into a high refractive index ATR crystal, also known as an internal reflection element (IRE), where it is reflected off the internal surface. This reflection creates an evanescent wave that penetrates a small distance into the sample in contact with the crystal. The interaction of the evanescent wave with the sample results in the absorption of specific wavelengths, producing a spectrum that can be used for qualitative and quantitative analysis.

ATR fiber probes extend the versatility and applicability of ATR spectroscopy by enabling in-situ and remote analysis of various chemical reactions.

Spectral ranges

The ATR technique is most commonly used in mid-IR spectroscopy, where vibrational transitions provide high absorption coefficients for molecular functional groups. In highly absorbing mixtures, ATR can also be used in near-infrared (NIR) spectroscopy and for measuring the absorption of electronic transitions in the ultraviolet-visible (UV-VIS) region. However, NIR and UV-VIS are less sensitive than MIR.

ATR Crystal Choice

Several factors influence the choice of ATR crystals, including the spectral range and chemical compatibility of the crystal material (**Table 1**):

1. **Spectral Range** of ATR crystal materials must be considered based on the application requirements.

2. **Chemical Compatibility** between the crystal material and the sample is critical, especially in harsh environments.

Diamond is suitable for most samples and is known for its robustness and high chemical resistance in any medium. However, a wide absorption gap at 2300-1900 cm^{-1} limits its use for some applications.

ZnSe has a wide working spectral and temperature range, but it is brittle and has a limited chemical compatibility. ZnSe dissolves in acidic and basic solutions and is not resistant to some complexing agents.

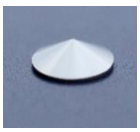
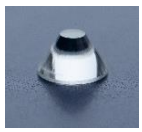
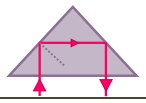
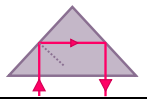
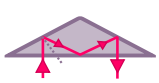
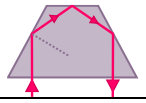
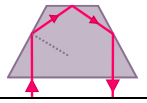
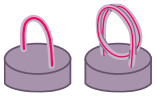
Germanium (Ge) is stable in non-oxidizing acids, but not In concentrated basic solutions and acids with oxidizing and complexing agents.

Silicon (Si) is hard and brittle and has a similar chemical compatibility to Ge.

Cubic Zirconia (ZrO_2, Zirconium oxide) and sapphire crystals can be used in NIR and MIR ranges while Sapphire is used in NIR and mostly in UV ATR probes. Both crystals are very hard and chemically stable except in concentrated alkalies.

Detachable Loops do not have a classical crystal shape and are presented in single, double or triple loops of fiber for enhanced sensitivity. They provide a cost-effective solution and are disposable. They are made from AgClBr polycrystalline fiber which interacts with acidic and basic solutions, S_2O_3 functional groups and other complexing groups. Loops are relatively fragile and can only be used for measurements in liquids.

Table 1 Overview of the available ATR Crystals for fiber probe spectroscopy at art photonics.

	Diamond	Zinc Selenide	Silicon	Germanium	Cubic Zirconia		Sapphire		Detachable Loops	
										
Scheme										
Reflections	**2**	**2**	**2**	**2**	**3**		**3**		Multiple	
Angle at Top	**90°**	**90°**	**120°**	**120°**	**60°**		**60°**		Not defined	
Angle of Incidence	**45°**	**45°**	**30°**	**30°**	**60°**		**60°**		Not defined	
Spectral range of ATR probe with the crystal	**600-1900 cm^{-1}**	**600-3100 cm^{-1}**	**600-3100 cm^{-1}**	**600-3100 cm^{-1}**	**1550-9000 cm-1**	**400-2200 nm**	**400-2200 nm**	**180-1300 nm**	**6500-1550 cm-1**	**2500-600 cm-1**
Fiber type in ATR probe with the crystal	**PIR**	**PIR**	**PIR**	**PIR**	**CIR**	**Silica NIR**	**Silica NIR**	**Silica UV**	**CIR**	**PIR**
Refractive index n_i of ATR crystal	**2.4**	**2.4**	**3.5**	**4**	**2.1**	**2.1**	**1.7**	**1.8**	**2.1**	**2.1**
Benefits of the crystal	Very hard, chemically inert	Uniform transmission over the entire mid-IR spectral range	Relatively hard, good chemical resistance	Uniform transmission over the entire mid-IR spectral range, good chemical resistance	Hard and chemically inert		Hard and chemically inert		Improved sensitivity by adding more turns; disposable tips	
Disadvantage of the crystal	Absorption bands in the range 2600-1900 cm-1	Soft and fragile, limited chemical resistance	Absorption bands in the spectral range below 1200 cm-1	Temperature sensitive; relatively soft	Limited transmission range		Limited transmission range		Soft and fragile, limited chemical resistance	
Chemical Resistance	Unlimited	pH 5-9	pH 0-10	pH 0-10	pH 0-12		pH 0-12		pH 5-9	
Limited Stability in	No limitations	Acids and alkalis, complexing agents	Strong alkalis, oxidizing and complexing agents	Strong alkalis, oxidizing and complexing agents	Strong alkalis		Strong alkalis		Acids & alkalis, complexing agents	

Conclusion

The choice of ATR crystal is important in fiber-based process spectroscopy, influencing the accuracy and reliability of spectroscopic measurements across different spectral ranges. By considering the spectral range and chemical compatibility of the crystal, users can optimize their ATR fiber probes for a wide range of applications.

For more detailed information, feel free to contact us:

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