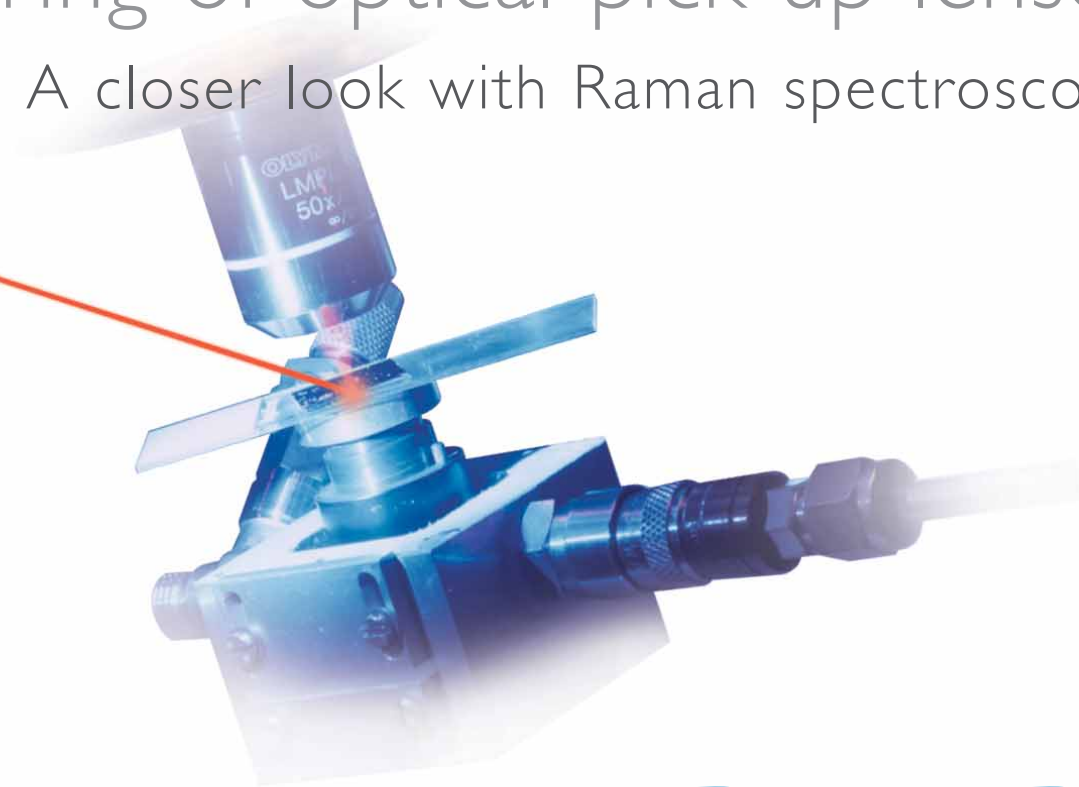
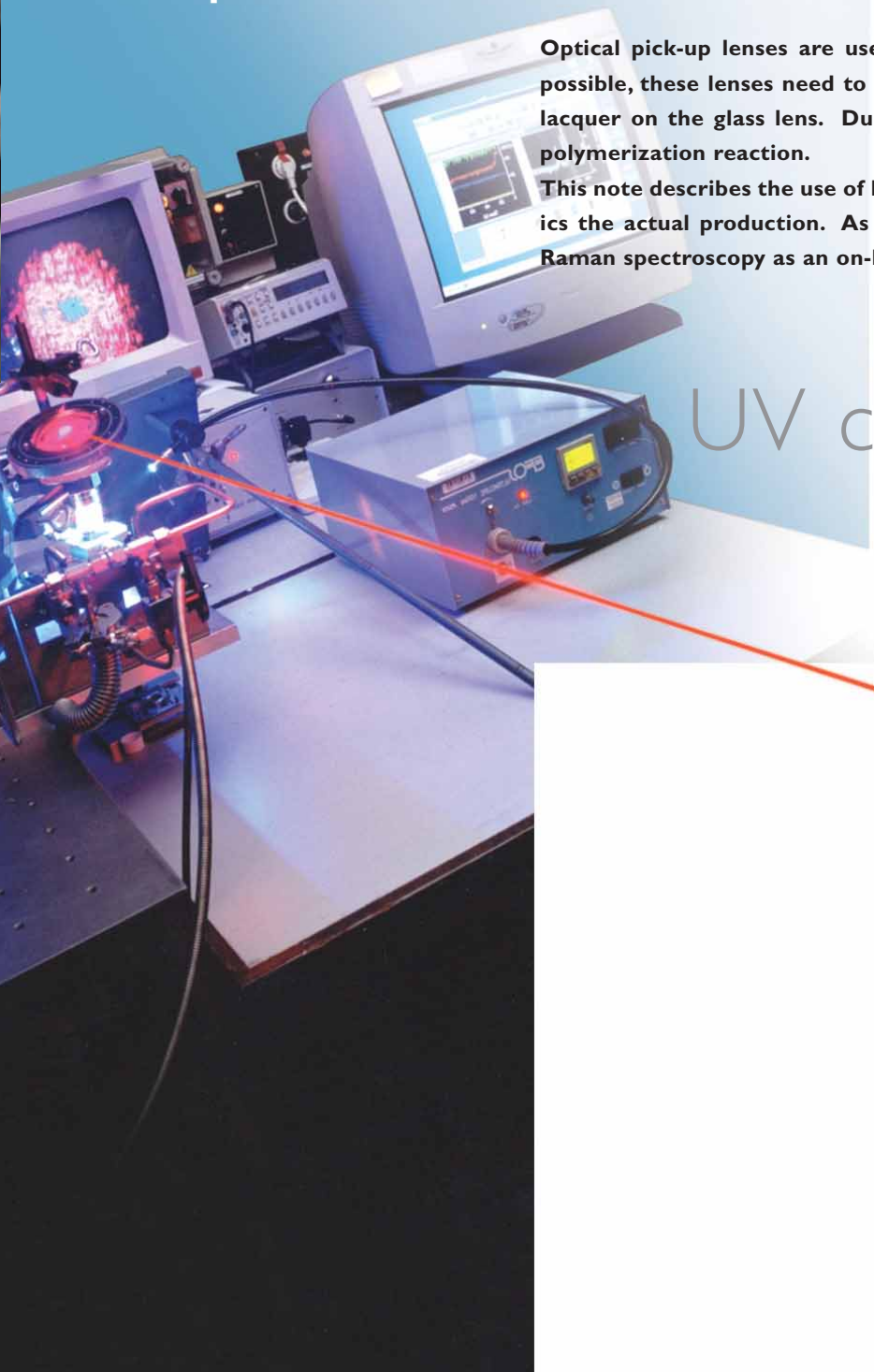


Optical pick-up lenses are used in optical storage devices such as CD, DVD and DVR. To obtain the highest information density possible, these lenses need to focus a laser-beam perfectly. The production of such lenses is based on UV-induced polymerization of lacquer on the glass lens. During this process the lacquer is completely surrounded by glass, which makes it difficult to study the polymerization reaction.

This note describes the use of Raman spectroscopy for optimizing and characterizing the lacquer polymerization in a set-up that mimics the actual production. As the reaction is followed from a distance through a glass window, the example shows the strength of Raman spectroscopy as an on-line analysis tool.

UV curing of optical pick-up lenses A closer look with Raman spectroscopy



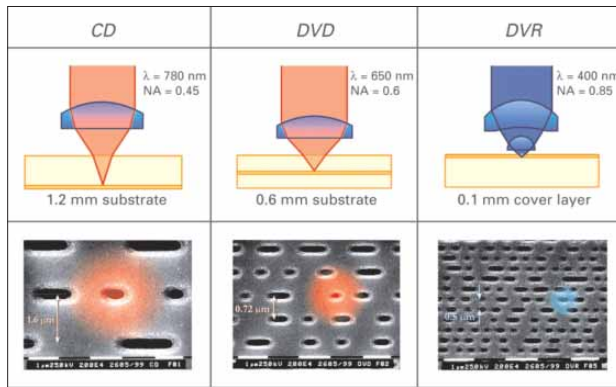


Fig. 1: Optical data storage possibilities.

Digital video recording

The new standard for optical data storage is Digital Video Recording (DVR). It should allow storage capacities of more than 30 Gbytes (4 hrs of video) on a surface the size of standard CD. To write and read this much information, the size of the laser spot should be kept to a minimum. This means that blue laser diodes and special aspheric lenses have to be used (fig. 1). Such lenses can be made from spherical lenses of conventional optical glass by correcting them by a thin (1 to 30 micrometer thick) aspherical layer of a transparent polymer.

Lens replication

The application of a correcting polymer layer is a three-step procedure (fig. 2). A small droplet of monomer (lacquer) is applied on the surface of a

glass lens. Subsequently, an aspherical mould is applied to shape the correction layer with nanometer precision. The layer is then exposed to UV radiation to obtain a solid and stable polymer (UV-curing), after which the mould can be released.

Raman spectroscopy

When laser light hits a surface, it gets reflected and scattered. Part of the light is scattered inelastically. The energy lost during the inelastic scattering contains chemical information about the irradiated material. This phenomenon forms the basis for Raman spectroscopy.

The energy transferred during scattering is typical for specific bonds in the material. This energy loss is normally translated to a wavenumber shift (cm^{-1}). An example: a typical carbon-carbon double

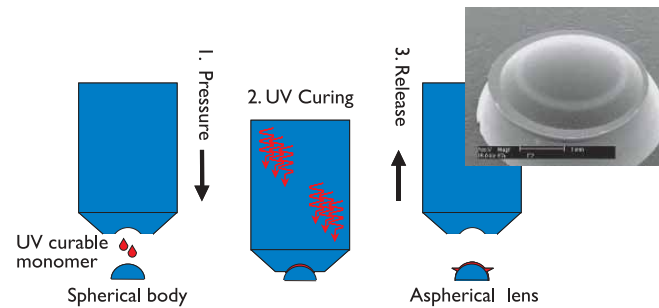
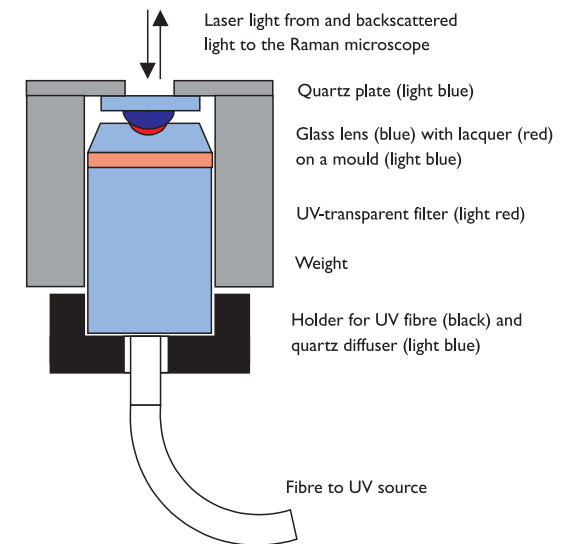


Fig. 2: The lens replication process and the final product (SEM-picture).

bond will result in inelastically scattered light at 1600 cm^{-1} from the laser wavelength. The amount of light is indicative for the concentration of a functional group in which the bond is present.

When the material of interest is visible to the eye, it can be reached by laser light. At the same time, the inelastic scatter from an object in water or behind glass can be analyzed without removing it from its environment. This means for the UV curing reaction that Raman analysis can be performed inside an actual production set-up when an optical window is present through which the lacquer can be analyzed. As the lens is transparent, a set-up as described in fig. 3 can be used to analyze lens production.

Fig. 3: Production system for aspheric lenses.



The Raman spectra of the lacquer contain a large amount of information about the functional groups in the material that change during polymerization. Fig. 4 shows a part of the spectra, taken before and after UV curing. The clearest differences between the spectra before and after UV curing are seen in the Raman bands at 1386 cm^{-1} , 1622 cm^{-1} and 1704 cm^{-1} . These are linked to changes in the C=C and C=O bonds that occur as a result of conversion of methacrylate groups during the polymerization.

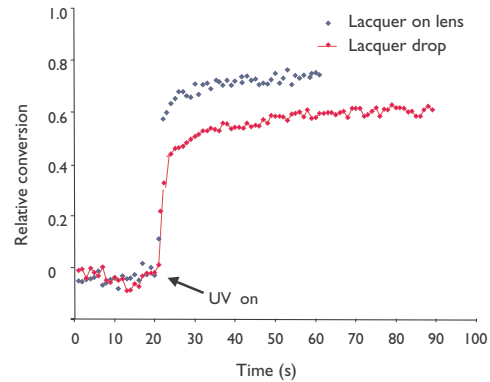
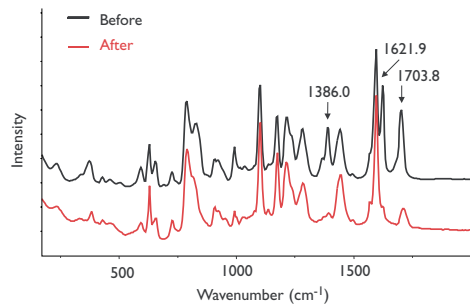


Fig. 5: Relative conversion of the monomer to polymer for a free drop and lacquer on a lens.

Fig. 4: Raman spectra before and after UV-curing. The position of characteristic Raman peaks is indicated.

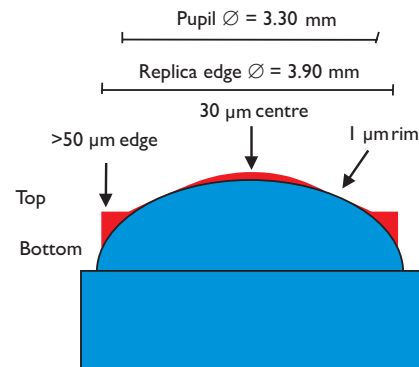


Reaction kinetics

A small drop of lacquer was UV cured on a lens in the set-up described in fig. 3. For comparison a drop of lacquer was cured in the same set-up without the lens present, leaving a large amount of free space around the drop. During the reaction a spectrum is recorded every 0.5 seconds. To obtain a clear indication of the conversion from monomer to polymer, the data is analyzed using a multivariate method that looks for changes in the spectrum that occur simultaneously. The relative conversion in time is shown in fig. 5 for both the free drop and the lacquer on the lens.

The reaction is too fast to follow the first part of the conversion during illumination, but the data clearly shows that the final degree of conversion is higher when the lens is present. This confirms that the actual production process cannot simply be studied on a free drop of lacquer. At the same time this example shows that the in-process analysis capability of Raman spectroscopy is very valuable.

Fig. 6: A description of the lens after photo-polymerization (polymer = red, glass = blue).



Remote analysis

In the replication process, the thickness of the lacquer layer varies strongly over the surface of the lens (fig. 6). At the position of the lens on which the mould rests (the rim) the thickness is less than 1 micrometer, while in the center of the lens a layer of 30 micrometer is present. It is possible that the conversion rate and final conversion degree are not constant over the lens surface.

To determine whether there are differences, the conversion during irradiation was recorded at different lens positions (fig. 7). Polymerization seems to occur with the same efficiency in the lens center and rim. The conversion on the edge of the lens is less complete.

A depth profile was made of the lens center and the lens edge to determine whether the degree of polymerization is the same throughout the layer. It turns out that the conversion is constant over the lacquer in the lens center, but on the bottom of the lens edge the conversion is lower (fig. 8). Other experiments indicate that this is due to exposure to oxygen (in air) during the polymerization on this position. Oxygen delays the radical-driven polymerization and results in a lower conversion rate with a similar amount of UV irradiation.

These examples show that Raman spectroscopy can be used for non-destructive and 3D characterization of material. Time-resolved measurements and in-process analysis are possible applications of the technique. Because glass or other transparent materials do not hinder this analysis method,

process optimization can be performed under conditions similar to those in production. Finally, because of its high spatial resolution, Raman spectroscopy allows non-destructive depth analysis in transparent materials with a maximum resolution of 1-2 micrometers.

Fig. 7: UV-induced conversion of monomer to polymer in time as a function of position on the lens. The latter values are averaged over the entire thickness of the lens.

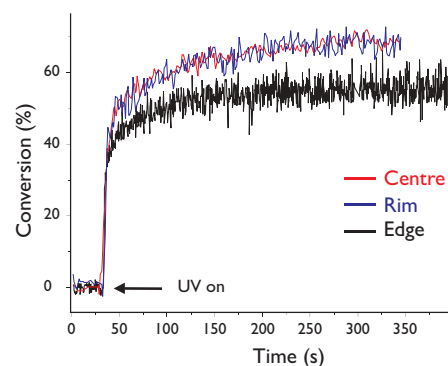
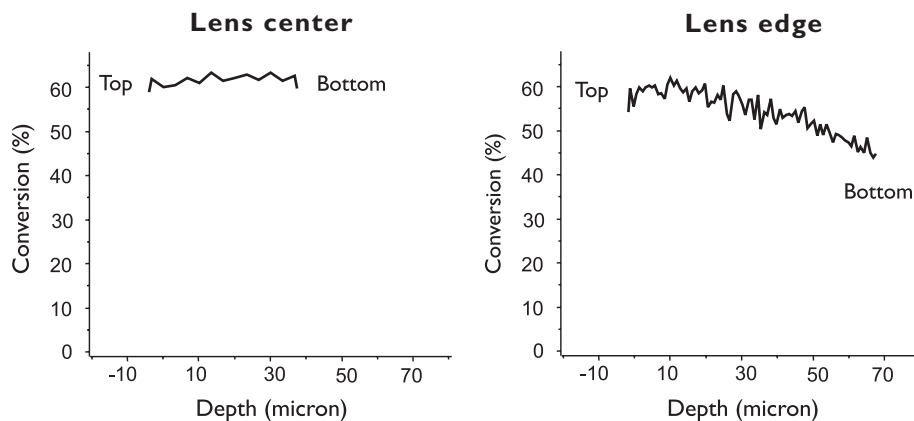


Fig. 8: Conversion as a function of depth at different lens positions. Confocal Raman microscopy was applied 1 hour after UV curing.



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