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Direct measurement of the complex refractive index in the extreme ultraviolet spectral region using diffraction from a nanosphere array

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Using extreme ultraviolet (XUV) radiation from a high harmonic source, we observe diffraction from a single-layer self-assembled hexagonal array of 196 ± 1.2 nm diameter polystyrene spheres. The Mie solution is used to predict the correct form factor for a single sphere and hence model the intensities of the observed diffraction peaks for the first three orders. By measuring the diffraction intensities in this way, we demonstrate a technique for obtaining the complex refractive index of a material at multiple wavelengths in the XUV from a single measurement. We present experimental results for polystyrene in the range of 25–30 nm. © *2008 American Institute of Physics*.

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High harmonic generation[1–3] (HHG) has the ability to generate high (10^{11} photons/s per harmonic) flux of extreme ultraviolet (XUV) radiation in a coherent,[4] low-divergence beam using a table-top laser source. This combination of flux and coherence allows new directions in nanoscale analysis.[5,6] This paper describes the use of a HHG radiation source in the measurement of the complex refractive index of polystyrene ($C_6H_5CH-CH_2$) using XUV diffraction from a single layer of 196 nm diameter polystyrene nanospheres, self-assembled into a hexagonal array. By fitting the Mie solution to Maxwell's equations to the intensity of the diffraction peaks, we demonstrate an accurate measurement of the complex refractive index at multiple XUV wavelengths using a single diffraction image. The measurement of the refractive index of a medium in this spectral region is difficult as the absorption lengths are on the order of nanometers, and alternate methods at this wavelength generally require a large number of reflectivity versus angle measurements.[7,8] This single-measurement technique is therefore of real practical benefit and is applicable for all wavelengths.

The data that exist for refractive indices in the XUV wavelength range,[9–11] described in the form $(1-\delta)+i(\beta)$, are for single elements and are predominantly extrapolated between data sets in the x-ray and UV wavelength range. It is known to feature significant errors in the XUV region. Typically, to calculate the refractive index for a compound, the refractive indices of the component elements[12,13] are combined in their constituent ratios using the noninteracting atom approximation,[9] and hence the molecular structure is not taken into account. The susceptibility of hydrogen changes significantly when it is bonded in a compound, especially at XUV wavelengths,[13] and a direct measurement is therefore required.

In this investigation, radiation from 1.5 mJ, 40 fs pulses centered at 800 nm from a Ti:sapphire laser is focused using a concave dielectric mirror ($R=1$ m) into a 3 cm long gas cell containing argon at a pressure of 10 mbar. The 23rd to 33rd harmonics are generated at wavelengths from 35 to 24 nm (36–51 eV). Two 100 nm thick aluminum foils are used to attenuate the laser by $\sim 10^8$ while transmitting $\sim 10^{-2}$ of the XUV radiation, which is focused using a Mo/Si multilayer mirror ($R=0.5$ m) to a spot size of 22 μm. The nanosphere array sample is positioned at the focus, and a water cooled x-ray charge coupled device (CCD) (Andor, 1024×1024 13 μm pixels) captures the scattered photons. The sample was fabricated by immersing a 50 nm thick silicon nitride membrane in water, forming a single layer of nanospheres (Duke Scientifics, density of 1.05 g/cm^3) on the water surface, then slowly removing the excess water to deposit the assembled nanospheres on the membrane. Well-ordered hexagonal arrays of monodisperse nanospheres can be easily created using this technique.[14,15] The average sphere size and uncertainty was calculated using a scanning electron microscope image of the sample and confirmed by the sample to detector distance and interference peak angles observed on the detector.

Figure 1 shows the far-field transmission diffraction pattern from the nanosphere array. Using the Scherrer formula,[16] the diffraction peak width (full width at half maximum) due to finite sample size is calculated to be ~1 CCD pixel. However, the observed diffraction peaks are broadened by two mechanisms. First, in the radial direction the peaks reflect the spectral structure of the source. Second, broadening in the axial direction is principally due to defects in the crystal lattice. The lack of rotational symmetry in the diffraction pattern results from a curved phase front at the focus of

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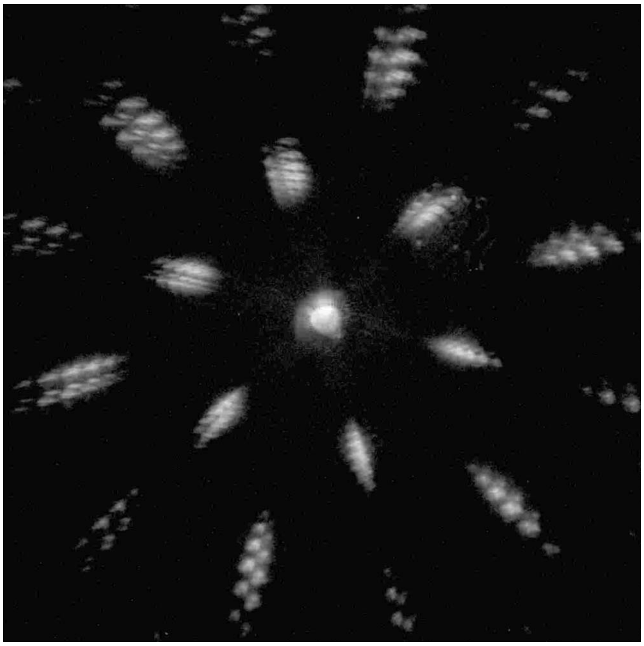

FIG. 1. Far-field diffraction pattern from the hexagonal array of 196 nm diameter polystyrene spheres for an integration period of 240 s. Maximum pixel count is ~40 000.

the XUV beam, a consequence of using a spherical mirror in an off-axis geometry.

The far-field diffraction pattern from a hexagonal array of spheres is a hexagonal array of delta functions multiplied by the scattering function from a single sphere. The diffraction peaks observed in Fig. 1 therefore effectively sample (at the diffraction angles) the angular distribution of light scattered from a single sphere, which can be calculated using the Mie solution. The Mie solution is an exact analytical result, which describes how light will interact with a simple object. The analytical results shown here have been calculated using the recursion method described in Ref. 17. The Mie scattering pattern is a function of the object's size (i.e., radius if spherical), its complex refractive index, and the wavelength of the incident light. The size and wavelengths are known experimental parameters, and hence knowledge of the intensity distribution enables a calculation of the complex refractive index. Measurement of the diffraction pattern provides the intensity at several discrete angles for each wavelength, and therefore this technique can be used to simultaneously determine the complex refractive index of the sphere for multiple wavelengths.

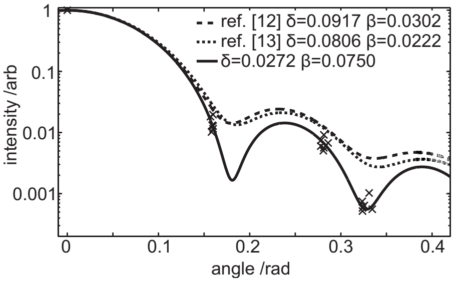

FIG. 2. Experimental interference peak intensities plotted against the theoretical angular distribution of 27.6 nm light scattered from a single sphere with refractive index taken from Refs. 12 and 13 and using the value determined in this paper. Theory and experiment are normalized to unity at $\theta=0$. Agreement for more than three orders of magnitude shows that the correct form factor has been determined.

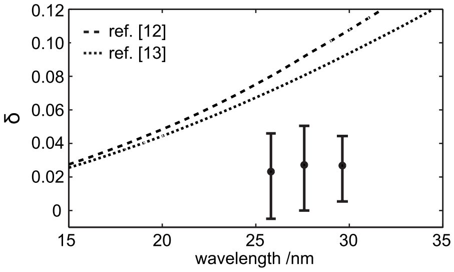

FIG. 3. A comparison of the experimentally measured value of δ with the theoretical values from Refs. 12 and 13.

In order to derive values for the complex index parameters δ and β, a nonlinear least-squares technique is used to fit the Mie scattering intensities to the measured diffraction peak intensities for the first three orders. This process has been performed at three of the generated harmonic wavelengths [31st (26.8 nm), 29th (27.6 nm), and 27th (29.6 nm)] using the same diffraction image. The limit of three harmonics is imposed by the narrow reflectivity of our multilayer XUV focusing mirror (Fraunhofer Institute). However, almost complete coverage of the XUV region would be possible using a combination of commercially available focusing mirrors, and therefore the determination of the refractive index is not limited to the wavelengths shown here. The fitting algorithm converges with fewer than 20 function calls to the Mie algorithm and always converges to the same solution for any sensible initial values for δ and β. The diffraction peak intensities were measured by finding the most intense pixel within each convoluted interference peak. Figure 2 shows experimental data points for the 29th harmonic at 27.6 nm, along with the theoretical scattering intensity distribution for a single sphere with $\delta=0.0272$ and $\beta=0.0750$. The distributions corresponding to the values of δ and β from Refs. 12 and 13 are shown for comparison.

Figures 3 and 4 show the experimentally measured δ and β and values calculated from the literature obtained from Refs. 12 and 13 plotted against wavelength. The trend for δ and β is predicted correctly by the references but not the magnitude. This discrepancy is likely to result primarily from ignoring the molecular structure of polystyrene.

This technique is extremely appropriate for high harmonic sources due to the wide range of wavelengths that can easily be generated. To interpret scattering data from a multiple wavelength source, an ordered structure of spheres is required. Without this, the sample would produce several superimposed continuous angular scattering distributions (one

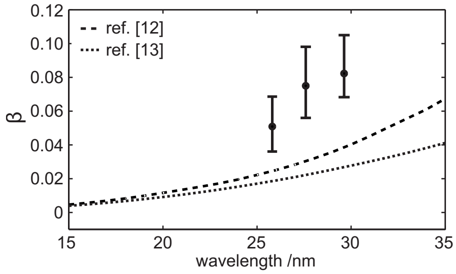

FIG. 4. A comparison of the experimentally measured value of β with the theoretical values from Refs. 12 and 13.

for each wavelength) that would not be possible to separate without additional wavelength selectivity. Although this technique requires a single crystal domain that is larger than the XUV focus, point defects can be tolerated as they do not significantly affect the intensity of the diffraction peaks. The intensities are instead extremely dependent on the complex refractive index of the material. This technique could be repeated for the shorter wavelengths that have been generated using HHG (Ref. 18) by simply using smaller spheres. In addition, changing the harmonic generation conditions[19] allows for the generated wavelengths to be shifted by up to 0.5 nm so that almost full wavelength coverage rather than discrete data points is possible. The analytical Mie solution is extendible to many shapes, for example, to hollow or coated spheres, and therefore this technique can also be used to investigate their properties. In this demonstration, the accuracy of the determined refractive index components is primarily limited by the curved phase front at the sample. An off-axis paraboloidal mirror would remove the systematic errors for the intensity of the diffraction at specific azimuth angles and significantly reduce the uncertainty in δ and β.

In conclusion, we have demonstrated XUV diffraction from a hexagonal array of 196 nm diameter polystyrene spheres using a high intensity, coherent, table-top source, and shown that the refractive index can be determined using the scattered intensity distribution. This technique emphasizes the applicability of a high harmonic XUV source for nanoscale analysis and is extensible to the measurement of the complex refractive index of a material across a range of wavelengths from a single diffraction image. This method will give new insights into the properties of materials in regions of high absorption and help create a more robust theoretical approach to the calculation of the refractive index of compounds. This technique is not limited to spherical object arrays. Any periodic object will diffract light in a way that is dependent on its complex refractive index, and hence further work will also investigate the application of this technique to other structures.

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[1] M. Lewenstein, P. Salieres, and A. L'Huillier, Phys. Rev. A **52**, 4747 (1995).

[2] R. Bartels, S. Backus, E. Zeek, L. Misoguti, G. Vdovin, I. P. Christov, M. M. Murnane, and H. C. Kapteyn, Nature (London) **406**, 164 (2000).

[3] P. M. Paul, E. S. Toma, P. Breger, G. Mullot, F. Auge, Ph. Balcou, H. G. Muller, and P. Agostini, Science **292**, 1689 (2001).

[4] R. A. Bartels, A. Paul, M. M. Murnane, H. C. Kapteyne, S. Backus, Y. Liu, D. T. Attwood, and C. Jacobson, Science **297**, 376 (2002).

[5] R. L. Sandberg, A. Paul, D. A. Raymondson, S. Hadrich, D. M. Gaudiosi, J. Holtsnider, R. I. Tobey, R. Cohen, M. M. Murnane, and H. C. Kapteyn, Phys. Rev. Lett. **99**, 098103 (2007).

[6] R. L. Sandberg, C. Song, P. W. Wachulak, D. A. Raymondson, A. Paul, B. Amirbekian, E. Lee, A. E. Sakdinawat, C. La-O-Vorakiat, M. C. Marconi, C. S. Menoni, M. M. Murnane, J. J. Rocca, H. C. Kapteyn, and J. Miao, Proc. Natl. Acad. Sci. U.S.A. **105**, 24 (2008).

[7] R. Soufli and E. M. Gullikson, Appl. Opt. **36**, 5499 (1997).

[8] I. A. Artioukov, B. R. Benware, J. J. Rocca, M. Forsythe, Yu. A. Upenskii, and A. V. Vinogradov, IEEE J. Quantum Electron. **5**, 1495 (1999).

[9] B. L. Henke, E. M. Gullikson, and J. C. Davis, At. Data Nucl. Data Tables **54**, 181 (1993).

[10] C. T. Chantler, J. Phys. Chem. Ref. Data **29**, 597 (2000).

[11] C. T. Chantler, J. Phys. Chem. Ref. Data **24**, 71 (1995).

[12] Centre for X-Ray Optics, http://henke.lbl.gov/optical_constants/getdb2.html, using Ref. 9 as the data source for individual elements.

[13] C. T. Chantler, K. Olsen, R. A. Dragoset, J. Chang, A. R. Kishore, S. A. Kotochigova, and D. S. Zucker, "X-ray form factor, attenuation and scattering tables (version 2.1)," http://physics.nist.gov/ffast, 2005, National Institute of Standards and Technology, Gaithersburg, MD, originally published as Refs. 10 and 11.

[14] C. F. Chau and T. Melvin, J. Micromech. Microeng. **18**, 064012 (2008).

[15] S. M. Weekes, F. Y. Ogrin, W. A. Murray, and P. S. Keatley, Langmuir **23**, 1057 (2007).

[16] A. L. Patterson, Phys. Rev. **56**, 978 (1939).

[17] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, Weinheim, 2004).

[18] E. A. Gibson, A. Paul, N. Wagner, R. Tobey, D. Gaudiosi, S. Backus, I. P. Christov, A. Aquila, E. M. Gullikson, D. T. Attwood, M. M. Murnane, and H. C. Kapteyn, Science **302**, 95 (2003).

[19] C. A. Froud, E. T. F. Rogers, M. Praeger, A. M. de Paula, D. C. Hanna, J. J. Baumberg, W. S. Brocklesby, and J. G. Frey, Opt. Lett. **31**, 374 (2006).