Low-voltage electron microscopy of polymer and organic molecular thin films

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Abstract

We have demonstrated the capabilities of a novel low-voltage electron microscope (LVEM) for imaging polymer and organic molecular thin films. The LVEM can operate in transmission electron microscopy, scanning transmission electron microscopy, scanning electron microscopy, and electron diffraction modes. The microscope operates at a nominal accelerating voltage of 5 kV and fits on a tabletop. A detailed discussion of the electron–sample interaction processes is presented, and the mean free path for total electron scattering was calculated to be 15 nm for organic samples at 5 kV.

The total end point dose for the destruction of crystallinity at 5 kV was estimated at $5 \times 10^{-4}$ and $3.5 \times 10^{-2}$ C/cm$^2$ for polyethylene and pentacene, respectively. These values are significantly lower than those measured at voltages greater than 100 kV.

A defocus series of colloidal gold particles allowed us to estimate the experimental contrast transfer function of the microscope. Images taken of several organic materials have shown high contrast for low atomic number elements and a resolution of 2.5 nm. The materials studied here include thin films of the organic semiconductor pentacene, triblock copolymer films, single-molecule dendrimers, electrospun polymer fibers and gold nanoparticles.

Keywords: Low-voltage electron microscopy; Polymer and organic molecular thin films

1. Introduction

There is considerable current interest in the use of polymer and organic molecular materials for device applications such as transistors, biosensors, and actuators [1]. For these materials to achieve their ultimate potential it is imperative to obtain detailed information about their microstructure, especially in the thin film forms central to technological applications. Our research group has been actively developing techniques for high-resolution electron optical examinations of polymers and organic materials, with particular emphasis on low-dose high-resolution electron microscopy (HREM) [2,3]. While this method of examining organic material structure has proven
to be particularly powerful, current generations of electron microscopes suffer from several problems. They are quite expensive (typically $500k–$1500k), require considerable amounts of space, and are time-consuming and fairly difficult to operate. Furthermore, the high voltages normally used in conventional electron microscopes (200–400 kV) provide little contrast when imaging thin films composed of low atomic number elements.

Recently, Delong Instruments in Brno, Czech Republic (www.dicomps.com) has developed an electron microscope that overcomes many of these disadvantages [4]. Their design consists of a tabletop-sized, low-voltage (\(5\) kV) electron microscope (LVEM) capable of operating in transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), scanning electron microscopy (SEM), and electron diffraction (ED) modes. Although there is a slight increase in the electron wavelength at these lower voltages (\(1.7 \times 10^{-2}\) nm at 5 kV vs \(1.6 \times 10^{-3}\) nm at 400 kV), there is still more than sufficient spatial resolution (2.5 nm) to obtain detailed information about sample structure. Furthermore, as we will discuss in fundamental detail, there is a significant increase in contrast when imaging at low voltage, suggesting that it may be possible to decrease the need for or perhaps even eliminate heavy metal staining altogether. In the LVEM, even small wrinkles in thin amorphous carbon support films near the copper grids can now be readily observed. For TEM imaging, the samples must be thin to allow the relatively slow electrons to pass through the sample: experiments have confirmed that the LVEM beam can successfully penetrate through 4 layers of polyethylene single crystals (\(\sim 40\) nm).

The LVEM has obtained high contrast TEM and STEM images from unstained polymer blends as long as the samples are sufficiently thin [5,6]. We have confirmed that the LVEM can successfully image a variety of polymer and organic molecular samples including block copolymers, polyethylene single crystals [4], dendrimer molecules, electrospun polymer fibers, gold nanocrystals, and thin films of the organic molecular semiconductor pentacene.

2. Experimental

2.1. Materials

Pentacene powder, as obtained from Aldrich, was thermally evaporated under a vacuum of \(5 \times 10^{-5}\) Torr onto an amorphous carbon-coated mica substrate held at room temperature. Polyethylene (120,000 g/mol, PDI 1.19) was crystallized at room temperature from a 0.1 wt% solution in tetrachloroethylene. 0.1 wt% of the triblock copolymer poly(styrene–isoprene–styrene) (SIS) was dissolved in toluene, atomized into droplets on amorphous carbon-coated mica and dried at room temperature for 24 h. Nylon 6.6 was electrospun onto amorphous carbon-coated mica using an AC electric field. Five nanometer colloidal gold particles were purchased from Aldrich in solution and then deposited onto carbon-coated mica. A drop of dendrimer solution in water was deposited onto carbon-coated mica. All samples deposited onto carbon-coated mica were then floated off of the mica onto deionized water for collection with Cu TEM grids.

2.2. Instrumentation

A low-voltage electron microscope from Delong Instruments (LVEM5) was used at a nominal operating voltage of 5 kV. The microscope’s design is considerably different than traditional TEMs and allows for significant miniaturization. The instrument is constructed with a small Schottky field-emission gun (FEG), permanent magnet condenser and objective lenses, electrostatic projector lenses, and a YAG screen for image acquisition using conventional light optics and a CCD camera. In TEM mode the magnification ranges from 1 to 150 kX with a resolution of 2.5 nm. The small volume of the vacuum chamber makes it possible to maintain an excellent vacuum (\(10^{-8}\) Torr at the FEG and \(10^{-7}\) near the sample) and provides for rapid sample exchange times (\(\sim 5\) min per sample). The pumping system includes two small ion pumps connected to the optical chamber, with a turbomolecular pump on the floor behind the unit. No cooling water is needed for operation of the microscope. The small
footprint of the device makes it particularly attractive for situations where space is at a premium. A photograph of the instrument and image acquisition system is shown in Fig. 1.

3. Results

3.1. Electron–sample interaction at 5 kV

When imaging the crystalline structure of organic samples by electron diffraction or HREM, the interaction of the electron beam with the sample is often a considerable problem to overcome. It is therefore important to characterize the stability of organic materials under electron irradiation. The resistance to electron irradiation is commonly determined in terms of the total dose of electrons (C/cm²) that causes a significant change to some measurable aspect of the sample structure; commonly the fading of intensity of Bragg reflections for crystalline samples. This method ignores beam damage to the amorphous component of some polymer and organic samples, but it has been accepted as a standard for quantifying electron–sample interactions in crystalline organics [7,8]. Fig. 2 shows a STEM micrograph of a polycrystalline pentacene thin film and a time series of electron diffraction patterns taken from the film. A crack in the film can be seen running through the image. At this focusing condition (zero defocus) the grain boundaries appear light and the single crystalline ~200 nm grains appear dark. Electron diffraction patterns were obtained from this sample as a function of time with a beam diameter slightly larger than the image width. Three strong rings are visible, which fade completely due to beam damage after 10 s. The rings correspond to the 0.46 nm (1 1 0) planes, 0.37 nm (2 0 0) planes and 0.31 nm (2 1 0) planes of thin film phase pentacene [9].

A number of previous studies have measured the interactions of electrons with organic matter at a variety of voltages [10–16]. A compilation of
results available from the literature is shown in Fig. 3. For organic polymers, there is a general correlation that samples with higher thermal stability tend to be more resistant to electron beam damage [15]. Most studies in the literature have been done at relatively high voltages (100–400 kV). However, recently data has been presented for beam damage at much lower voltages (0.2–1.0 kV) [10]. As shown in Fig. 3, there is little information available about the beam sensitivity of organic materials voltages between 1 and 100 kV. The recent data from Stevens et al.

![Graph showing critical dose vs. beam voltage for organics](image)

**Fig. 3.** Compilation of electron beam sensitivity of organic materials from the literature. Recent studies by Stevens et al. [10] on copper phthalocyanine (CuPc) and the aromatic compound coronene suggest that the damage may be more significant near 5 kV than at either higher or lower voltages. The solid curve is a fit of Eq. (5) to the CuPc data with the ionization energy $U = 285$ eV and an ionization fraction $f = 0.004$.

indicate that there is an increase in beam sensitivity as the voltage decreases from near 100 kV, but below 1 kV this trend turns around, and there is then a decrease in sensitivity at the lowest voltages.

Experiments with the LVEM have confirmed that fading of the Bragg reflections of PE single crystals can be observed within 1 s with a beam current of 5 nA, for a beam diameter of 35 $\mu$m. This corresponds to an estimated total end point dose of $5 \times 10^{-4}$ C/cm². This data point is shown in Fig. 3, and is reasonably consistent with the trend of measurements at higher voltages. Similar experiments with pentacene have given an estimated end-point dose of $0.035 \pm 0.01$ C/cm² at 5 kV, compared with $0.25 \pm 0.05$ C/cm² at 400 kV.

The theory of inelastic collisions was examined by Gryzinski [17], who calculated the probability of carbon K-shell ionization as a function of incident electron energy. This calculation based on classical Coulomb collision theory predicts a maximum ionization cross-section at an incident electron energy slightly higher than the K-shell ionization energy. The cross-section decreases as the incident energy increases. As the incident electron energy is decreased in the range of the ionization energy, the ionization cross-section also decreases. The cross-section for K-shell ionization by electrons is

$$Q = n(\sigma_0 / U^2)g(x),$$  \(1\)

where $n$ is the number of K-shell electrons, $\sigma_0 = 6.56 \times 10^{-14}$ eV cm², $g(x)$ is of the form

$$g(x) = \frac{1}{x} \left( \frac{x - 1}{x + 1} \right)^{3/2} \left( 1 + \frac{2}{3} \left( 1 - \frac{1}{2x} \right) \right)$$  \(2\)

and $x$ is the ratio of the kinetic energy of the incident electron $E$ to the binding energy of the orbital electron $U$,

$$x = E/U.$$  \(3\)

The dose $d$ of electrons that cause a single K-shell ionization is therefore

$$d = e/Q$$  \(4\)

and the critical dose $D$ for damage caused by K-shell ionization is

$$D = fd,$$  \(5\)
where $f$ is the fraction of ionized molecules necessary to cause beam damage. The theoretical ionization damage dose $D$ vs. the incident electron energy $E$ (from Eqs. (1)–(5)) is overlaid with the critical dose data compiled from the literature (Fig. 3). The curve is fit to the CuPc critical dose vs. incident electron energy data from Ref. [10] with the carbon K-shell ionization energy of $U = 285$ eV. One CuPc molecule contains 64 carbon K-shell electrons. The fraction of ionized CuPc carbon atoms necessary to cause beam damage is $f = 0.004$ in the fit. This value corresponds to one K-shell ionization for every four CuPc molecules. Howie and coworkers [16] found that beam damage occurred in films of $p$-terphenyl, a more beam resistant molecule than CuPc, at a carbon atom ionization fraction of $f = 0.02$. The above analysis assumes that beam damage is due to carbon K-shell ionization alone. The theoretical curve in Fig. 3 correlates with the CuPc data well, indicating that carbon K-shell ionization may be the dominant process causing beam damage in this material and possibly other crystalline organics as well.

Fig. 3 shows that beam damage to crystalline samples is most significant at electron energies near 5 kV. The interaction of electrons with the sample at this intermediate voltage is very strong, and this is precisely why the LVEM produces high contrast in TEM images from organic samples. We have measured the electron mean free path in organic materials at ~5 kV from experimental images. Polyethylene single crystals with a thickness of 10 nm were imaged in TEM mode, and the intensity profiles in the images were related to the known sample mass-thickness. The ratio between the number of scattered electrons $n$ per incident electron $n_0$ is equal to the measured intensity at the film $I$ for a beam of incident intensity $I_0$. The expected relationship between this ratio and the product of the density $\rho$ and the thickness $t$ (mass-thickness) is given by

$$n/n_0 = I/I_0 = \exp[-S_p \rho t] = \exp[-t/A_t].$$  

Fig. 4. Mean free path for total electron scattering calculated using the mass thickness contrast observed in TEM as a function of beam voltage, and assuming a nominal density of 1 gm/cm$^3$. The low value of the mean free path at 5 kV means there will be high contrast for small variations in mass-thickness.

Hence, the mass-thickness contrast parameter $S_p$ is inversely proportional to the total mean free path $A_t$. The relationship between $A_t$, $S_p$ and the total cross section $\sigma_t$ is given by

$$A_t = \frac{1}{S_p \rho} = \frac{A}{N_A \sigma_t \rho},$$  

where $A$ is the atomic weight and $N_A$ is Avogadro’s number. We have calculated the characteristic mass thickness contrast coefficient $S_p$ to be 0.69 cm$^2$/µg from experimental images. Using an estimate of 1 gm/cm$^3$ for the density, this corresponds to an estimated mean free path for total electron scattering $A_t$ of 15 nm for organic samples at 5 kV [18]. This result is plotted with other values of the mean free path calculated from mass thickness contrast coefficients from the literature in Fig. 4 [19,20]. This relatively low value of the mean free path means that for samples with constant thickness, high contrast will be obtained from small variations in density. For example, for 5% contrast in the LVEM bright field image we will only need to have a difference in density between the phases of 0.07 g/cm$^3$. This means that the usual need to stain polymers for enhanced contrast in the TEM (typically done with osmium or ruthenium tetraoxide) may not be necessary with the LVEM. It also emphasizes the need to...
obtain support films that are as thin as possible when operating the LVEM in transmission mode.

A fundamental question that remains open is the quantitative variation in total inelastic scattering with decreasing electron energy. Observations of samples imaged in the LVEM have given intriguing, qualitative clues about how these interactions differ as the voltage is decreased. For example, for sufficiently thin specimens (10–20 nm) it seems that there is a significant decrease in the inelastic scattering. Specifically, the images at low thickness are sharper, and do not show the characteristic halos that are typical of chromatic aberration. With thick samples there is a loss of resolution and the halos characteristic of chromatic aberration become more obvious. We also anticipate that there may be changes with damage sensitivity in polymer thin films. There have been some reports of substantially increased electron beam resistance for thin crystalline polymers [21], while no such changes were observed in nanocrystalline molecular films [22].

3.2. LVEM of polymer and organic molecular thin films

3.2.1. Pentacene

We have used the LVEM to study thin films of the organic molecular semiconductor pentacene. We have obtained high contrast images of extremely thin (~20 nm) films of thermally evaporated pentacene. The image in Fig. 5(a) shows a polycrystalline film of thin film phase pentacene on top of which another layer of crystals has begun to nucleate and grow. Successful processing of pentacene and other conductive organic materials for electronic applications demands detailed structural information about the number and nature of lattice defects present, such as grain boundaries and dislocations, as well as knowledge of the crystal structure and orientation. The high contrast of the LVEM, as well its selected area diffraction capabilities, make it ideal for such use.

3.2.2. Block copolymers

There is considerable current interest in block copolymers, particularly in multi-block systems with intricate morphologies. The LVEM would significantly enhance studies of block copolymer morphology since it has more than adequate resolution and would have high contrast for subtle differences in sample density, making it possible to minimize or eliminate staining. A LVEM image of an unstained SIS droplet is shown in Fig. 5(b). Note the high contrast between the blocks, which have a density difference of only ~0.1 g/cm³. SIS is known to be difficult to image in traditional high-voltage microscopes, although measurable contrast between the blocks has been achieved with appropriate defocusing conditions [23,24]. Some block-copolymers of current interest, such as PS-PMMA, do show high contrast when imaged with high-voltage electrons. This is due to radiation damage of the PMMA block, which rapidly degrades with increased electron exposure [25–27]. With minimum dose techniques, image contrast of such samples could be directly related to density and thickness changes across the sample, without the effects of mass loss.

3.2.3. Dendrimers

Dendrimers are highly branched polymers that radiate from a central core. Characteristics of dendrimers include low intrinsic viscosity, high solubility and high reactivity. The high reactivity is a result of the large number of chain ends, each of which may contain a functional group. There are many potential applications for dendrimers currently being investigated, including dendrimers for drug and gene delivery to cells, micro-catalysts and adhesives.

We have imaged Generation 5 (G5) and Generation 7 (G7) poly(amidoamine) (PAMAM) dendrimers [28] without staining. Reports of TEM imaging of individual dendrimer molecules have used staining to enhance contrast [29]. Fig. 5(c) shows a LVEM image of unstained G7 dendrimers which are approximately 8 nm in diameter. Here the contrast is due to the local changes in mass-thickness caused by the dendrimer. Complementary imaging using an AFM operating in tapping mode has confirmed that the dendrimers are pancake shaped, with a height of 1–2 nm above the amorphous carbon substrate. Excellent contrast is
obtained for this small change in sample height at relatively constant density.

3.2.4. Electrospun nanofibers

There are several groups [30–32], including our own, actively investigating the use of electrospinning to create polymer fibers with nanometer dimensions. We have shown that oscillating fields create filaments with novel structures [33]. However, the precise relationship between processing conditions (such as concentration, electric field magnitude, electric field frequency) remains elusive. The LVEM provides reasonably rapid turn around in microstructural analysis and should be particularly useful in this regard. An LVEM image of electrospun Nylon 6,6 beaded fibers on an amorphous carbon substrate is shown in Fig. 5(d). The beaded fibers were produced by an AC electric field across the nylon solution and the substrate. Beaded fibers may improve the mechanical properties of composites depending on the bead size relative to the fiber diameter and the number of beads per fiber [34].

3.3. Estimation of the experimental contrast transfer function (CTF)

Because the objective lenses are permanent magnets, focusing is accomplished by adjusting the accelerating voltage or physical displacement of the sample in the z-direction. By performing a z-height defocus series on amorphous thin films or small particles it was possible to estimate the contrast transfer function of the microscope. An under focused image of 5 nm colloidal gold nanoparticles, and its corresponding digital Fast Fourier Transform (FFT), is shown in Fig. 6. The contrast in the FFT (light and dark rings) is
directly related to the two dimensional CTF of the microscope. We have plotted the positions \( \langle k \rangle \) of the first and second zeros in the CTF measured from FFT images of colloidal gold nanoparticles as a function of defocus \( (D_f) \). The CTF is well approximated by the function \( \sin \left( \frac{w}{C_{s}l^3k^4} \right) \), where \( w \) is defined as

\[
\chi(k, D_f) = \pi D_f \lambda^2 + \frac{1}{2} \pi C_s \lambda^3 k^4,
\]

where \( k \) is the position in reciprocal space, \( D_f \) is the defocus of the microscope, \( \lambda \) is the wavelength and \( C_s \) is the spherical aberration coefficient of the objective lens [35,36]. Fig. 7 shows a plot of the experimental positions of the first (red dots) and second (blue dots) zeros in the CTF measured from the first and second zeros in the FFT images. The red and blue lines are the theoretical first and second zeros, respectively, obtained by fitting the above equation to the data. In the fit, a linear scaling parameter, which relates the defocus in units of focus knob turn (degrees) to \( z \)-axis height (nm), was varied to obtain the best match between the equation and the data. The value of this scaling parameter as determined from the fit was \( D_f \) (nm) = 1070 \( D_f \) (deg). A value of 0.64 mm was used for \( C_s \), known from the manufacturer’s lens design. The function \( \sin[\chi] \) is plotted with the data in order to see the variations in contrast at different length scales \( (k) \) expected with changes in defocus \( (D_f) \). When the CTF is negative (dark regions) positive phase contrast results, and atoms or electron-dense regions appear dark against a bright background. The opposite is true when the CTF is positive (white regions), and when it is zero there is no information in the image at the particular value of \( k \).

The ultimate resolution of the microscope found at the Scherzer defocus condition can be determined by solving Eq. \( (8) \) for the maximum value of \( k \) at the first zero in the function \( \sin[\chi] \). The resolution at Scherzer defocus is [36]

\[
d = \frac{1}{k_{\text{max}}} = 0.66(C_s \lambda^3)^{1/4}
\]

with \( C_s \) taken to be 0.64 mm and the electron wavelength at 5 kV equal to 0.0173 nm the resolution of the microscope at Scherzer defocus is 0.9 nm. The true microscope resolution is limited by other factors than just the spherical

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**Fig. 6.** Underfocused TEM image of 5 nm colloidal gold particles taken in the LVEM. The contrast variations in the FFT, inset, can be related to the two-dimensional contrast transfer function of the microscope.

**Fig. 7.** Plot of the experimental contrast transfer function of the microscope. The data points are the positions of the first and second zeros in contrast measured from FFTs of gold particles (see Fig. 6). The data is plotted on top of the function \( \sin[\chi] \) which was fit to the data by varying the value of \( D_f \).
aberration alone, however. Other aberrations, especially chromatic aberration, limit the microscope resolution at the highest magnifications. FFTs taken from experimental LVTEM images of ultra-thin amorphous carbon films at Scherzer defocus (−125 nm), where the position of the first zero in the CTF is at a maximum value of $k$, give a resolution of $d = 1/k_{\text{max}} = 2.5$ nm. In Section 3.1 of this paper we discussed the qualitative effects of specimen thickness on the apparent chromatic aberration present in TEM images. It will be of interest in future studies to quantify the effect of specimen thickness on the amount of chromatic aberration and its effect on the microscope resolution.

4. Conclusions

Our results to date have clearly shown the broad range of samples that can be successfully imaged with the LVEM. The ability to obtain TEM, SEM, and STEM images from the same region of a single sample makes it possible to corroborate information by changing the mode of data acquisition. The relatively limited penetration capabilities (50 nm) present some new challenges for sample preparation, but these are not a fundamental problem to overcome in practice. We have had excellent results by dispersing the objects of interest onto ultrathin (<10 nm) amorphous carbon coated single crystals of mica, followed by floating onto deionized water for collection on copper TEM support grids. The shapes of bigger objects can also be easily seen, so the instrument is expected to be quite valuable for looking at inorganic clusters, block copolymers, liquid crystalline samples and biological structures in the nanometer size range.

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