

# Diamondoid Coating Enables Disruptive Approach for Chemical and Magnetic Imaging with 10nm Spatial Resolution

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Diamondoids are unique molecular-scale diamonds with fascinating new properties such as negative electron affinity (NEA) and short electron mean free paths. A thin layer of diamondoids deposited on a cathode is able to act as an electron monochromator, reducing the energy spread of photo-emitted electrons from a surface. This property can be applied effectively to improve the spatial resolution in x-ray photoemission electron microscopy (X-PEEM), which is limited by chromatic aberration of the electron optics. In this paper we present X-PEEM measurements reaching the technological relevant spatial resolution of 10-nm without the need of expensive and complex corrective optics. Our results provide a simple approach to image surface chemical and magnetic information at nanometer scales by employing diamondoid nano materials.

Keywords: diamondoids, electron microscopy, X-ray absorption, electron emission

Diamond is a wide band gap insulator that combines material properties such as high refractive index, mechanical hardness, biocompatibility and high thermal conductance, making it attractive for applications like drug delivery<sup>1,2</sup>, mechanical coatings<sup>3</sup>, and electron emitters<sup>4</sup>. Recently, applications for nanometer scale diamond particles (5-50nm), often referred to as nano-diamonds, have developed rapidly in the bio-medical<sup>1</sup> and quantum computing field<sup>5</sup>. Even smaller, molecular-scale diamonds are known as “diamondoids”, consisting of only a few diamond unit cells. Higher diamondoids consist of four or more cages in a molecule, and were first isolated from petroleum by a group of scientists at Chevron<sup>6,7,8</sup>. Measurements of tetramantane thiol monolayers on Au and Ag surfaces recently revealed that these molecules are negative electron affinity (NEA) materials, where the vacuum level lies below the lowest unoccupied molecular orbital (LUMO). This property combined with strong electron phonon scattering and extremely short mean free path in diamondoid caused monochromatization of secondary electrons emitted from a metal surface<sup>9</sup>. The electron emission spectrum is characterized by a sharp peak with a bandwidth of 0.3eV (FWHM), which surpasses the value that is obtained on bulk diamond<sup>10,11</sup>. This particular property generated strong interest in the photo-cathode community since it opens the door to a completely new and disruptive approach to design new generations of photo-cathodes with superior emission properties. However, applications which are based on the ability to effectively transform electron energy with as little as a single layer of diamondoids have not yet been demonstrated.

In x-ray photoemission electron microscopy (X-PEEM), a sample is illuminated using polarized and monochromatic X-rays typically generated by a synchrotron. The absorption of X-rays leads to emission of photo- and secondary electrons from the sample surface acting as a cathode. Because of its element, chemical and spin structure specificity it is used by researchers from a variety of disciplines for composition mapping and analysis<sup>12-18</sup>. However, the photoexcited electrons from the sample surface tend to have a broad energy distribution, limiting the spatial resolution to 25 nm or more due to chromatic aberration within the electron lens system<sup>19,20,21,22</sup>. This puts X-PEEM at a disadvantage when compared to related techniques such as X-ray transmission or diffraction microscopy<sup>23,24</sup>. Ultraviolet excitation could be used to limit the energy spread to 1 eV or less to obtain 10 nm spatial resolution<sup>19</sup>, however at the cost of elemental, chemical and magnetic sensitivity. Another approach is to introduce corrective electron optics into the microscope<sup>19,20,21,22</sup>. However, this comes at significant costs (>\$1M) compared to conventional PEEM (~\$100k) and makes the operation much more complex. In this paper we show how the effect of chromatic aberrations in X-PEEM can be minimized without compromising the functionality or the setup of the instrument at minimal cost using a thin diamondoid coating, by a layer of [121]tetramantane-thiol<sup>10,11,25</sup>, which form a self-assembled monolayer (SAM) on selected metal surfaces<sup>26,27,28,29,30</sup>. Our findings represent the first successful application of diamondoids to effectively improve the performance of an electron cathode.

To illustrate the idea behind our approach we will briefly describe the effects of the diamondoid coating on the energy distribution of the electrons emitted from the surface in an x-ray absorption spectroscopy setup as it is shown in Figure 1. Soft X-rays with photon energies of several hundred electron volts impinge on the surface. At certain photon energies characteristic for the elements present in the sample, the absorption of soft X-rays will occur through the resonant excitation of core level electrons into empty valence states (1). Subsequent recombination of the excited state causes the emission of an Auger electron (2). Both the Auger and the photoelectron will travel to the surface, lose their energy through inelastic scattering and generate a cascade of secondary electrons (3) with a wide energy distribution ( $>5$  eV) as shown by the black curve in Figure 1 (taken from<sup>31</sup>). Without the diamondoid coatings these secondary electrons are directly emitted into the vacuum and contribute to the image formation in X-PEEM. To limit the effects of chromatic aberration of the lens system an aperture is typically mounted in the back focal plane of the objective lens that rejects 90% or more of the electrons but at the same time reduces the effect of chromatic aberrations<sup>20,21</sup>. Using apertures with a diameter of 10 - 20  $\mu\text{m}$  one can achieve a spatial resolution of about 25 nm<sup>19,22</sup>, while still maintaining practical image intensity. Upon coating the sample surface with a monolayer of diamondoids, the energy distribution of the emitted electrons, however, changes dramatically. The negative electron affinity and efficient electron scattering process cause the electrons passing through the diamondoid surface layer to be scattered and to relax to the lowest unoccupied molecular orbital (4) before they are emitted into the vacuum<sup>10,11</sup>. Consequently their energy distribution is much smaller as shown by the red curve in Figure 1., which has been acquired using X-rays with a photon energy of 700 eV from a diamondoid coated Au surface using a Scienta hemispherical analyzer. To benchmark, we also compare this new data with earlier data acquired at 55 eV<sup>10</sup> (green), as well as data obtained using a UV source<sup>31</sup> (blue line). The electron energy mono-chromatization effect still functions as effectively at 700 eV, which is an order of magnitude higher than earlier experiments using 55 eV photons<sup>10</sup>. In summary, we find similar energy spreads after excitation with 700eV X-ray photons on a diamondoid covered surface as after excitation with 5eV UV photons from a bare surface. We can therefore expect that the effect of chromatic aberration on the spatial resolution and ultimately the spatial resolution observed using diamondoid covered samples in X-PEEM should be similar to the spatial resolution that can be obtained in a UV-PEEM, which is 10nm.

For our experiments we used the state of art PEEM3 microscope<sup>22</sup> installed at the Advanced Light Source, a soft X-ray synchrotron in Berkeley, CA (USA)<sup>32</sup>. Images with magnetic contrast were obtained using X-ray magnetic circular dichroism (XMCD)<sup>33</sup>. For this purpose the energy of the incoming X-rays is tuned to the L absorption resonance where the XMCD effect is most pronounced and two images are acquired with opposite circular polarization of the incident X-rays and subtracted from each other. In our case we tuned the energy to the Co L<sub>3</sub> resonance at 778.1 eV since all our magnetic samples are based on

Cobalt. The resulting images do not contain topographic or chemical but only magnetic information<sup>12</sup>. An image consisting of only topographic and work function contrast can be obtained in a similar manner by computing the sum of the two images. Images with chemical contrast as shown later were acquired by subtracting images taken on and off resonance, in this case the carbon  $\pi^*$  resonance at 284.7eV with linear polarization. No additional image processing has been applied. Although not always shown the images exhibited contrast on different length scales from a few tens of nanometer up to several hundreds of nanometer. Structures larger than 1 $\mu$ m were used as reference and the contrast transfer was assumed to be one on these length scales, which is a reasonable assumption since the intrinsic resolution of the microscope is reported to be of the order of 25nm<sup>22</sup>.

For our experiments we obtained X-PEEM images from different samples exhibit, magnetic, topographic and chemical contrast. Co/Pd multilayer samples were prepared using sputter deposition at Hitachi Global Storage Technologies<sup>34</sup>. The layer structure of the magnetic material was ([Co(0.5 nm)Pd(0.7 nm)]x40), producing magnetic films that will align the magnetization perpendicular to the sample surface. The same layered structured was used for the bit-patterned media (BPM) sample. To obtain a BPM sample, however, 35 nm sized Si islands separated by 25 nm grooves, which are also 25 nm deep, were prepared using a lithographic process<sup>31,35</sup>. The magnetic material was then deposited on top. Finally a sample consisting of Au nanoparticles was prepared by depositing Poly-L-Lysine (PLL) on top of silicon. Au nanoparticles of sizes 10 nm $\pm$ 3 nm were then deposited on top of PLL and coated with 3nm Ti and 3nm Ag. All of the samples were coated with diamondoids using a method described in reference<sup>26,27</sup> and that has been shown to be able to reliably obtain monolayer coating on metal surfaces<sup>9</sup>. Due to a thin layer of Ag, diamondoid nanowires were formed on top of the nanoparticle sample at sizes ranging from 20 nm to 100 nm<sup>36</sup>, as detected by scanning electron microscopy. This hybrid organic-inorganic material incorporates organic linkers together with inorganic clusters to form highly crystalline materials such as Nano ribbons, nanowires, and lamellar sheets<sup>37</sup>

We first present results obtained on larger structures ( $\sim$ 120nm). For this purpose we acquired images of magnetic domains in a continuous Co/Pd multilayer sample. The magnetization in adjacent domains points either out or into the sample surface creating the a domain pattern that can be observed using the XMCD effect. The domain size distribution is very homogeneous in these samples over large areas<sup>34</sup>, which is why they are often used as a standard for magnetic imaging<sup>38</sup>. We systematically decreased the spatial resolution of the microscope by reducing the acceleration voltage and increasing the size of the back focal aperture from its optimal condition<sup>35</sup> and measured the effect of diamondoid coating on the spatial resolution. By reducing the acceleration voltage, the effect of chromatic aberration - which is proportional to  $\Delta E/E$  - is increased, and by opening the back focal aperture, a larger bandwidth is accepted

into the microscope, also increasing the effect of chromatic aberration on the image. For example, using a low acceleration voltage of 10 kV (5 kV/mm), as shown in Figure 2a, the magnetic contrast is barely visible, while the diamondoid coating leads to a significant recovery of the image contrast, so that the main characteristics of the domain pattern can still be observed. The quantitative differences between the two cases (small/large back focal aperture) depending on the acceleration voltage are shown in Figures 2b and 2c. We find that the count rate per image pixel increases in the diamondoid coated samples, although the integrated incoming photon flux measured by a Au grid in front of the microscope was identical for all measurements. This observation is a direct consequence of the 0.6eV reduction in work function caused by the [121] tetramantane-thiol monolayer<sup>39</sup> as well as the increased transfer through the back focal aperture due to the reduced energy spread of the electron yield. In addition, we observe that the image contrast between the white and dark areas is consistently increased by diamondoid coating using identical exposure times as demonstrated in Figure 2c. Again, this effect is clearly visible in the images as shown in Figure 2a. At these operating conditions, i.e. low photon flux and low acceleration voltage, the diamondoid coating allows us to resolve magnetic domains that are 120 nm in size, which is not possible when using uncoated samples. These are the very conditions necessary for the analysis of polymers and biological samples that are sensitive to X-ray beam damage. Some of these samples will often degrade within a minute of exposure to X-ray, (see e.g. reference 14 and 15) and the ability to increase the observable contrast that can be obtained in short times is crucial to such studies. The diamondoid coatings will therefore allow researchers to study such sensitive samples with improved spatial resolution<sup>40</sup>.

We now determine the intrinsic resolution limit of the microscope and show the effect of the diamondoids under these conditions. We obtained images of the magnetic domain pattern as well as the topography of so called magnetic bit patterned media (BPM). We first acquired images with the diamondoid SAM on top of the sample, and then evaporated the diamondoid layer by annealing at 200 degree Celsius for 10 minutes allowing us to take an image of the same spot with and without the diamondoid coating. Using magnetic XMCD contrast we show in the top row of figure 3 that our before and after images were indeed taken from the same spot on the sample. Since the maximum contrast that can be obtained using the XMCD effect is of the order of 10% we already observe an improvement of the image contrast for the 60nm BPM sample. The beneficial effect of the diamondoid coating can be recognized in these images, e.g. in the area marked with a red rectangle exhibiting a checkerboard domain pattern. The effect becomes much clearer when the topography images are analyzed. The topography image on the right of Figure 3a shows uninterrupted vertical and horizontal lines that represent 25 nm grooves as well as 35 nm islands. These grooves can hardly be resolved by eye in the image on the left, obtained without diamondoids, indicating that the spatial resolution of the microscope is indeed approximately 25 nm and also that the diamondoid coating improves the spatial resolution beyond this point. Note that in both cases

the topography images show work function contrast as well. The patchy contrast that appears on a length scale of 100s of nm is due to variation in work function, probably caused by residual photochemical left behind after the lift-off process. Altogether, the images with magnetic and topographic contrast as well as the line scans clearly show that the diamondoid coating is able to improve the spatial resolution of X-PEEM well beyond its current limits of 25nm.

The final step is to show that a spatial resolution of 10 nm can be achieved using diamondoid coating in X-PEEM with element specific chemical contrast, which is one of the capabilities making X-PEEM microscopy so attractive. Figure 4a shows an X-PEEM image of a diamondoid coated sample containing Au nanoparticles (diameter  $(10 \pm 3)$  nm) as well as Ag nanowires ranging from 20nm to 100nm in size as determined independently by scanning electron microscopy (not shown). The images were obtained by tuning the X-ray energy to the C- $\pi^*$  resonance (284.5 eV) and normalizing them to images obtained off resonance at (280 eV). The resulting contrast, shows that the nanoparticles density of Carbon  $\pi^*$  orbitals varies across the surface and is increased on the nanoparticles. This observation is further corroborated by acquiring local X-ray absorption spectra on the nanoparticles and normalizing them to absorption spectra acquired on the background. Such a spectrum is shown in figure 4b. It exhibits a distinct peak at 284.5eV which is indicative of the presence of  $\pi^*$  orbitals, in combination with the existence of a  $sp^2$  bonding situation. Hence the contrast shown in Figure 4a is of true chemical origin. A magnified image of a small area, as indicated by the red box in Figure 4b, is shown in Figure 4c revealing four round objects 10–13 nm in size. These objects represent the original Au nanoparticles that were deposited on the surface. Horizontal and vertical linescans (Figure 4d) confirm their size and spacing to be ranging from 10–13 nm. Again the origin of the contrast is the increased density of  $sp^2$  hybridized carbon. Changes of the chemical coordination of carbon can be observed on a length scale of 10nm. We can therefore conclude that we were able to obtain images with chemical contrast and 10nm spatial resolution in X-PEEM.

The spatial resolution of a microscope can be uniquely quantified measuring its transfer function, i.e. the evolution of contrast for different sized objects. We therefore determined the contrast transfer in our X-PEEM from different samples as discussed before using identical imaging conditions (20 kV acceleration voltage/10  $\mu$ m aperture). For this purpose we calculated the image contrast of different objects with different lateral size and normalized this value to the contrast observed for much larger structures with identical origin, like larger magnetic domains away from the patterned area or “large bundles” of nanowires. The transfer functions obtained for samples with and without diamondoid coating are shown on a so called Bode (magnitude) plot, where the amplitude of the contrast transfer is plotted versus the spatial frequency, that is  $1/(2d)$ . The typical behavior of the transfer function, when plotted this way, is that it is constant, or only slowly decreases up to a certain frequency and then drops off linearly

until it reaches zero. The length scale for which the contrast can still be detected is identified as the spatial resolution of the optical system. The first observation is that the contrast transfer is practically unaffected until a spatial frequency of  $5 \mu\text{m}^{-1}$  (100 nm objects) in the coated samples, while the contrast in images without coating already shows a significant decrease of about 50% at this length scale. Without the diamondoid coating the contrast transfer (red) decays quickly and reaches 3% at 25 nm. On the other hand the coated samples consistently show a contrast increase by a factor of  $\sim 2.5$ . In summary, we find that at 25 nm the contrast transfer is still significant on samples with the diamondoid coating reaching its limit at 10 nm.

In summary we find that diamondoid SAMs coatings: (1) Increase the transfer function of the microscope on average by a factor of 2.2-2.5. (2) Allow us to obtain images with improved contrast of samples that are sensitive to X-rays or electric fields without sacrificing resolution. (3) Improve the ultimate spatial resolution to 10nm and reduce exposure times overall, which are particularly relevant for time-resolved microscopy studies and studies where small contrasts originating from interfaces or small variations in chemistry across surfaces are of interest. In this study we focused on metal surfaces covered with diamondoids via a thiol bond. However, first results indicate that similar stable bindings can be achieved on oxide surfaces<sup>41,42</sup> or directly on Si surfaces<sup>43</sup> without the need to deposit a metallic sticking layer first. This will extend the application of this simple and inexpensive “X-PEEM resolution booster” to many more systems of interest.

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### **Figure captions:**

#### **Figure 1**

Effect of the diamondoid coating on energy distribution of the secondary electron yield following X-ray absorption. (1) Resonant absorption of a soft X-ray photon by excitation of a core level electron into an empty valence state. (2) Recombination of excited state through emission of an Auger electron. (3) Generation of secondary electrons through inelastic scattering of Auger electron and Photo electron. (4) Mono-chromatization of secondary electrons in diamondoid layer followed by emission from lowest unoccupied molecular orbital (LUMO). Inset shows energy distribution of secondary electrons ejected from a metal (Au) surface after excitation by 700 eV X-ray photons with (red) and without (black) the diamondoid coating. Also shown, the energy distribution of secondary electrons after excitation by 5 eV UV-photons (blue) without diamondoid coating and 55 eV extreme UV photons (green) with diamondoid coating.

#### **Figure 2**

X-PEEM images of magnetic domains in a Co/Pd multilayer obtained at an acceleration voltage of 10kV and using a back focal aperture of 35 $\mu$ m. The image on the left hand side was obtained without the diamondoid coating the image on the right hand side with the diamondoid coating. In both cases an exposure time of 80 seconds was chosen.

### Figure 3

X-PEEM images of magnetic domains (top row) and the topography (bottom row) of Co/Pd bit patterned media with a period of 60nm/ (35nm bits/25nm spacing). The total exposure times was 300 seconds. The left column shows images without the diamondoid coating and the right column images obtained with diamondoid coating. Magnetic and topographic images were obtained at the same area of the sample.

### Figure 4

**a** X-PEEM image of the same sample obtained using chemical contrast mechanism at the carbon  $\pi^*$  resonance. The nanowires as well as the nanoparticles (see inset) can clearly be identified and resolved. An exposure time of 120 seconds was used

**b** XAS spectrum obtained from the nanowires, which appear white in a. The peak at 284.7eV is indication of the presence of  $\pi^*$ -orbitals, indicative of  $sp^2$  bonding. The image in a was obtained using this photon energy.

**c** Horizontal linescan across the inset in b. The spacing between the particles is 13 nm

**d** Vertical linescan across the inset in b. The size of the particles is determined to be 10.5 nm and 13.5 nm.

### Figure 5

Optical transfer function determined using coated (black) and uncoated (red) samples. In all cases the acceleration voltage has been set to 20 kV and the 15  $\mu\text{m}$  aperture has been used. Data has been obtained using magnetic, topographic and chemical contrast using the samples discussed in Figure 2–4, The diamondoid coating leads to a consistent increase in contrast transfer of 2.5. Maximum contrast is obtained up to structure sizes of 100 nm ( $5 \mu\text{m}^{-1}$ ), while the contrast transfer of uncoated samples is already reduced by a factor of two. Ultimately 10nm structures can be resolved (3% contrast transfer) using diamondoid coating.