Optical Microscopy

The gemstone was examined with both an inspection microscope and a metallographic microscope. Some chip damage was observed at the apex of the back of the gemstone opposite the front facet, as shown in Fig. 4 and the upper image of Fig.5. The remaining images show the material to be a single crystal, as desired, but contrary to the Diamond Nexus Lab claim. Polish marks can be observed in several of the images.

The surface is subject to mounds of organic materials which move about with repeated washings, but are very hard to totally remove. This is probably because zirconia wants to be a monoclinic structure crystal, not cubic, below 1000°C. The inclusion of yttrium stabilizes it as a cubic crystal, but the surfaces tend to be high energy, somewhat unstable, surfaces. Dirt, usually organic material, on the surface helps to lower the surface energy and has a tendency to cling quite tenaciously to it. Corundum has less tendency to cling to organic material.

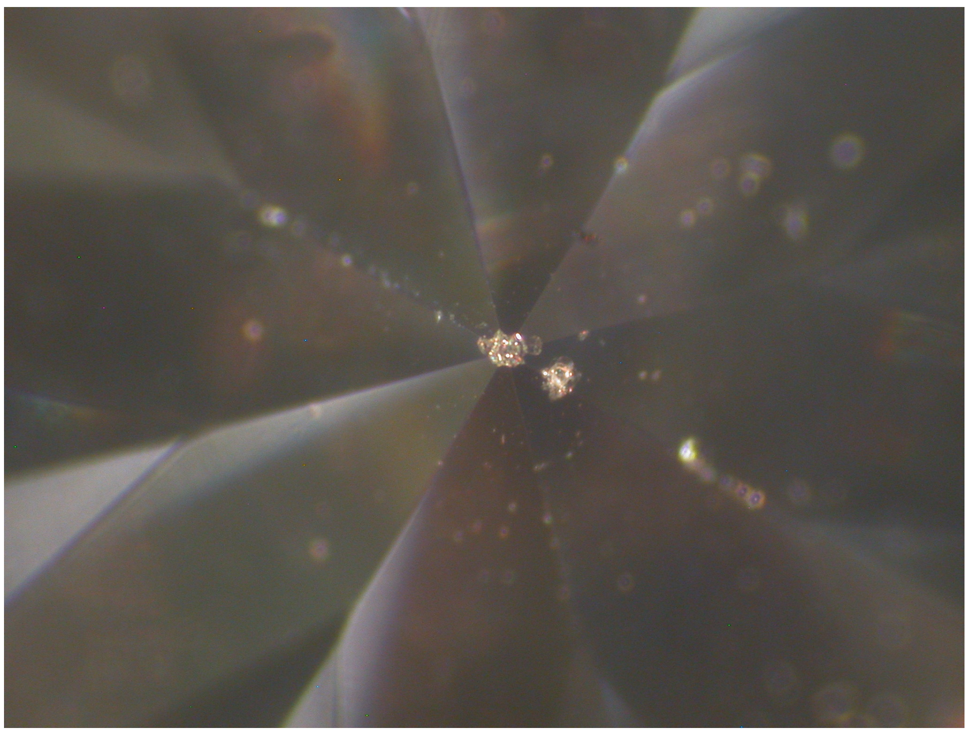

Fig. 4. Chip damage at the apex of the back side of the gemstone, opposite the front facet, is shown at a magnification of 58 times as-printed. The limited depth of field of higher magnification optical microscopy does not allow the series of chips along the facet edges radiating from the apex to we seen in focus. They appear here as white areas.

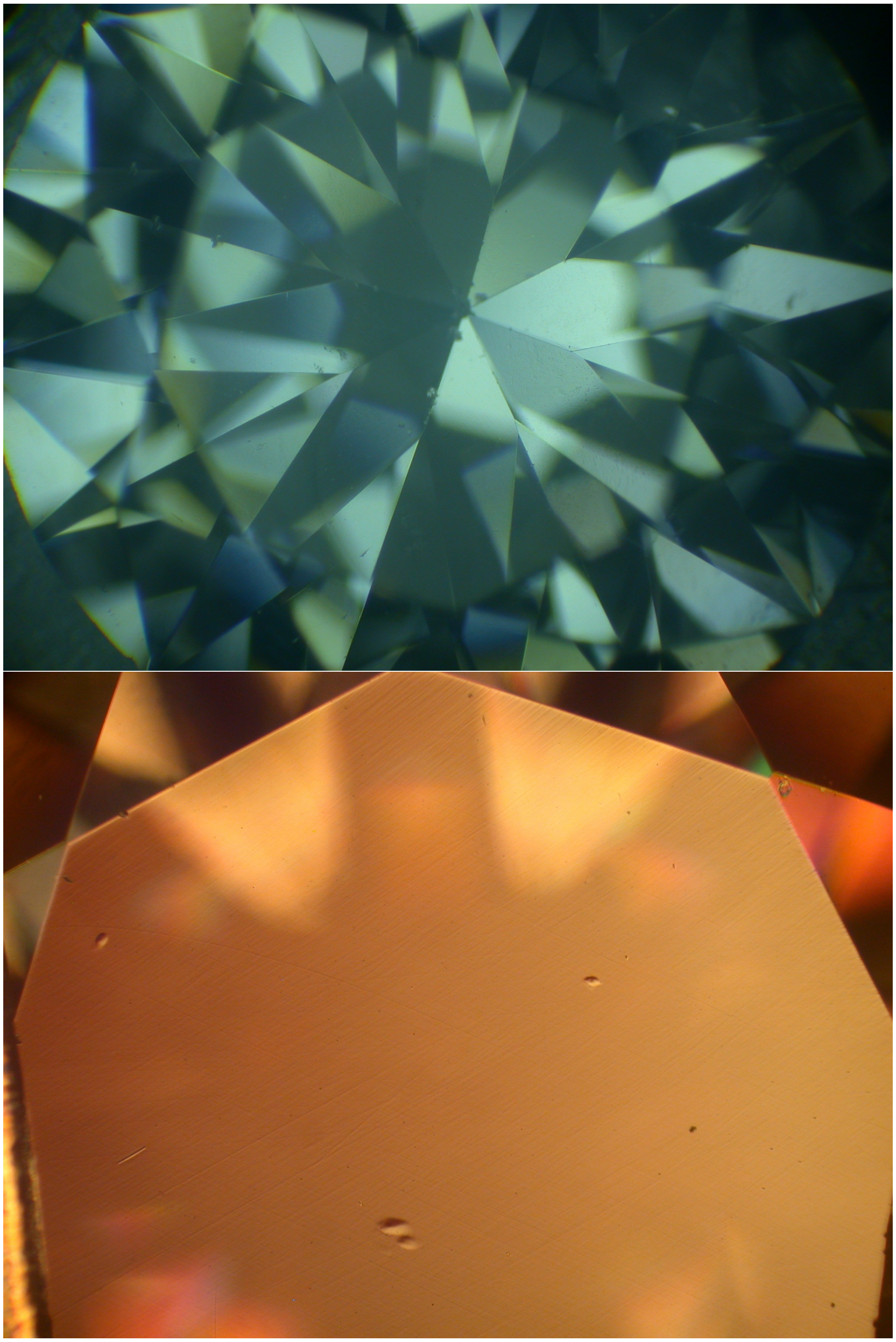

Fig. 5. The upper image is made with an inspection microscope which has a fairly great depth of field. The gemstone is examined through the front facet and the damage at the back apex is visible. The magnification is 25 times as-printed. The lower image is made on a metallographic microscope, which has a narrow depth of field and is focused on the front facet. The small mounds on the surface are likely organic and carbonaceous materials that cling to this high-energy surface and prove difficult to clean off. The polishing marks are just visible. The magnification is 95 times as-printed.

Fig. 6. The front facet of the gemstone as observed by a metallographic microscope. These images were made using Nomarski differential interference phase constrast, which changes the color, but helps to resolve surface features with respect to height differences, chemical differences, and optical index of refraction differences. The two mounds shown here were surface contamination, which moved and changed with each cleaning of the surface. The upper image has a magnification of 185 times, while the lower image is magnified 348 times as-printed.

XPS Results

The x-ray photoelectron spectroscopy (XPS) analysis was performed over an elliptical area irradiated by the low-energy (1487 eV) monochromatic aluminum Kα x-ray with a major axis of 1.2 mm and a minor axis of 0.6 mm. This is an area of approximately 0.6 mm^2. A wide-angle input lens, hemispherical mirror analyzer, and a multi-channel detector make the spectrometer very efficient. The depth of the analyzed volume is about 8 nm, which is determined by the small mean-free path of the emitted photoelectrons. The elemental survey spectra cover the binding energy range from 0 to 1100 eV, with a step size of 0.5 eV. This step size, with the monochromator, the moderate analyzed area size, and a high signal-to-noise ratio, improves the quantitative accuracy and sensitivity beyond industry standards.

The XPS system consists of a turbomolecularly pumped introduction chamber, an ion pumped sample preparation chamber, and an analysis chamber which is also ion pumped. When samples are inserted into the Analysis Chamber, they pass through the Preparation Chamber, which decreases the exposure of the Analysis Chamber to water vapor and hydrocarbons from the Introduction Chamber. We also make a practice of segregating the samples of different customers to minimize cross contamination.

Samples can be argon ion bombarded to etch material from a surface when the composition as a function of depth from the original surface is to be examined. The ion gun operates at 4 KeV and uses a rastered inert argon ion beam.

The quantitative elemental results obtained on the front facet of the 0.56 carat round brilliant cut Signature Series diamond simulant gemstone are presented in Table 1. Many elements were found in the outer 8 nm of the surface of the gemstone, but the primary elements are zirconium, yttrium, oxygen, and carbon. These are the elements one expects to see on a yttrium-stabilized cubic zirconia surface. Some of the carbon is due to the hydrocarbons absorbed from air that are found in a very thin layer on almost any surface. Cubic zirconia also commonly has a high carbon internal impurity concentration and some of the carbon tends to diffuse to any surface nearby, unless it is tied up in bonds with the zirconium as zirconium carbide. None of this surface carbon was in the form of zirconium carbide.

Fluorine in the form of fluoride, phosphorus, some nitrogen in the form of organic nitrogen or metal nitride, iron, copper, zinc, and silicon were all found on the surface. Some of these may be residues left by polishing compounds or other environments to which the gemstone was exposed. Zirconium will form a fluoride, a nitride, and a nitrate.

The only one of these minor concentration elements which may have a beneficial effect upon the surface might be the fluorine in the fluoride form. As fluoride treatment hardens tooth enamel, perhaps a fluoride treatment was performed to harden the yttrium-stabilized cubic zirconia surface. This would make it more scratch resistant, but might also make it more susceptible to shallow surface fractures upon impact. This may account for the several shallow chips we found on this stone and that I have seen on some photos of other diamond simulant gemstones provided recently by Diamond Nexus Labs. There is downside to hardening the surface with a fluoride treatment, even if it works. ZrF_4 is soluble in cold water and decomposes in hot water. Perhaps what is actually formed is an oxyfluoride and this might not be water soluble.

A hardness of 9.1 on the Mohs scale is claimed by Diamond Nexus Labs on their diamond simulants, but the hardness of cubic zirconia itself is about 8. A fluoride treatment might make the surface harder, but I have no knowledge that this is the case. The claim of a hardness of 9.1 may be as unfounded as the claim that corundum was coated on and infused into the surface of this diamond simulant gemstone. We know that corundum is not present on the surface because no aluminum was detected on the surface. It would be interesting to test the hardness of this gemstone, but we do not perform that test in our laboratory. If it does test out as a 9.1 hardness on the Mohs scale, it would be interesting to see if the same gemstone would retain such a hardness after submersion for a period of time in hot water.

I also etched 10 nanometers (nm, 10^{-9} meters) deep into the front facet of the gemstone and determined the composition at that depth. We found only zirconium, yttrium, oxygen, carbon, a greatly reduced concentration of fluorine, and a trace of copper. About one-fifth of the carbon is in the form of a carbide. Both zirconium and yttrium form carbides, namely ZrC and YC_2. ZrC is harder than yttrium-stabilized cubic zirconia. Thus, the portion of the carbon impurities in the gemstone in the form of carbide may also serve to make it harder. Given that some carbide is present, there is a slight excess of oxygen, if all the oxygen is bonded as oxide. It is therefore likely that some of the oxygen is due to hydroxyl groups, OH^-. There were about 0.30 yttrium atoms for each zirconium atom at this 10 nm depth.

These results may be compared to those for the DNL diamond simulant gemstone I ordered from DNL in April 2007, which are also presented in Table 1. The results are very similar, though a few more surface impurities were found on the surface of the 2012 DNL gemstone. At depths of 5.6 and 11.3 nm into the April 2007 DNL gemstone, only carbon, oxygen, zirconium, and yttrium were detected. At both depths, the ratio of yttrium to zirconium was about 0.3. There was more carbon at these depths in the DNL gemstone of 2012 compared to that of 2007. These results are compared to those on a Signity white cubic zirconia gemstone ordered in 2007. In that case the issue of surface contamination was eliminated with a deeper argon ion sputter to a depth of 31 nm. Only carbon, oxygen, zirconium, and yttrium were detected at this depth slightly below the surface. The yttrium to zirconium ratio was once again about 0.3. The carbon concentration was higher in the subsurface region of this gemstone than in either of the DNL gemstones.

TABLE 1. Atomic concentrations of the elements in atomic percent in the Diamond Nexus Labs (DNL) Signature Series diamond simulant surface and near surface determined by XPS compared to the 2007 DNL diamond simulant and the known Signity yttrium-stabilized cubic zirconia.

Element	March 2012 DNL		April 2007 DNL			2007 Signity
	Surface, Alcohol Cleaned	**10 nm Etched by Argon Ions**	**Surface, Alcohol Cleaned**	**5.6 nm Etched by Argon Ions**	**11.3 nm Etched by Argon Ions**	**31 nm Etched by Argon Ions**
Carbon, C	28.74	15.42	30.34	11.93	7.41	24.17
Oxygen, O	50.13	54.89	48.62	57.37	59.16	48.73
Zirconium, Zr	12.95	22.43	14.27	23.69	25.49	20.58
Yttrium, Y	2.97	6.71	3.66	7.02	7.94	6.51
Fluorine, F (fluoride)	1.62	0.52	0.38			
Phosphorus, P	1.34		0.79			
Nitrogen, N (organic or nitride)	0.83					
Nitrogen, N (nitrate)	0.71					
Iron, Fe	0.23					
Copper, Cu	0.22	0.03	0.25			
Zinc, Zn	0.14		0.19			
Tin, Sn		0.71				
Silicon, Si	0.12		0.78			
Y:Zr Ratio	0.229	0.299	0.256	0.296	0.311	0.316

Conclusions

The Diamond Nexus Labs 0.56 carat round brilliant cut Signature Series diamond simulant gemstone, ordered by Anna Palka on 27 March 2012, is not coated with a layer of corundum (another name for alumina or aluminum oxide), despite Diamond Nexus Lab's claim that it was. The gemstone is a standard yttrium-stabilized cubic zirconia with some surface impurities. The gemstone is not at all unusual for yttrium-stabilized cubic zirconia. This DNL diamond simulant was compared to the DNL diamond simulant ordered by Charles Anderson on 25 April 2007 and was found to be very similar in composition. The 2007 DNL diamond simulant did not have a surface coating on it either and was also yttrium-stabilized cubic zirconia. These DNL diamond simulant surface and near surface compositions of the 2007 and 2012 gemstones were compared to the composition of the known Signity cubic zirconia white gemstone and found to be highly similar to it.

The particular gemstone we analyzed had some shallow chips at apexes and along some facet edges. There was no evidence that the material is polycrystalline as claimed by Diamond Nexus Labs. That would be a very bad quality, were it true.