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SUBJ XPS Analysis of the Surface of a Diamond Nexus Labs Diamond Simulant, SKU GS0006, Princess Cut Loose Gemstone, 0.56 Carats

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Summary

The principal results of the x-ray photoelectron spectroscopy (XPS) analysis of the broad front facet of the princess cut diamond simulant from Diamond Nexus Labs are:

- The principal elements of the gemstone are zirconium, yttrium, and oxygen, so the gemstone is a common cubic zirconia. The ratios of Zr, Y, and O near the surface vary slightly with depth. At a depth of about 11.3 nm the formula of the cubic zirconia is $Zr\,Y_{0.311}\,O_{2.321}$, which means the oxide is oxygen-deficient at 0.941 times the stoichiometric value.

- No Hf, Fe, Ni, or Co were detected, despite Diamond Nexus Labs listing them as present in the FAQs page of their website.

- At concentrations of 0.8 at.% or less, P, Si, Sn, F, Cu, and Zn were detected on the surface of the gemstone, but the removal of a mere 5.6 nm of surface material using argon ion sputtering in a vacuum system with a pressure of about 3×10^{-9} Torr completely removed all of these elements. These elements were simply surface contamination of the gemstone.

- Immediately after sputtering the surface with argon ions, the carbon concentration was almost zero in the initial scan of the binding energy range for the measurement of the atomic concentrations of the elements. During the measurement, we observed the carbon concentration on the surface to increase. This increase was due to the adsorption of hydrocarbons in the XPS system, despite its great vacuum, onto the surface. Cubic zirconia is very inclined to bond to carbon and hydrocarbons.

- An excess of oxygen was measured on the surface. This may be due to the reaction which can cause cubic zirconia to become cloudy and is observed here in an early stage due to the great surface sensitivity of XPS. Zirconia has a tendency to react with water and carbon dioxide. At a depth of 5.6 nm after argon ion sputtering, the ratio of the measured oxygen to the stoichiometric oxygen concentration for the measured amounts of Zr and Y was 0.991. At a depth of 11.3 nm, this ratio was an oxygen-deficient 0.941. Many artificially formed bulk oxides are oxygen-deficient.

Sample

The 0.56 carat princess cut loose gemstone was ordered from Diamond Nexus Labs on 25 April 2007 by me. It was shipped in a small zip locked plastic bag, which was inside a small gold box in a blue draw-string bag. The gemstone was identified with the SKU of GS0006 on the packing slip. The gemstone was placed in an ultrasonic cleaner and cleaned with Micro, then rinsed with IPA to provide a clean surface for the XPS analysis. The gemstone is shown in Fig. 1 below.

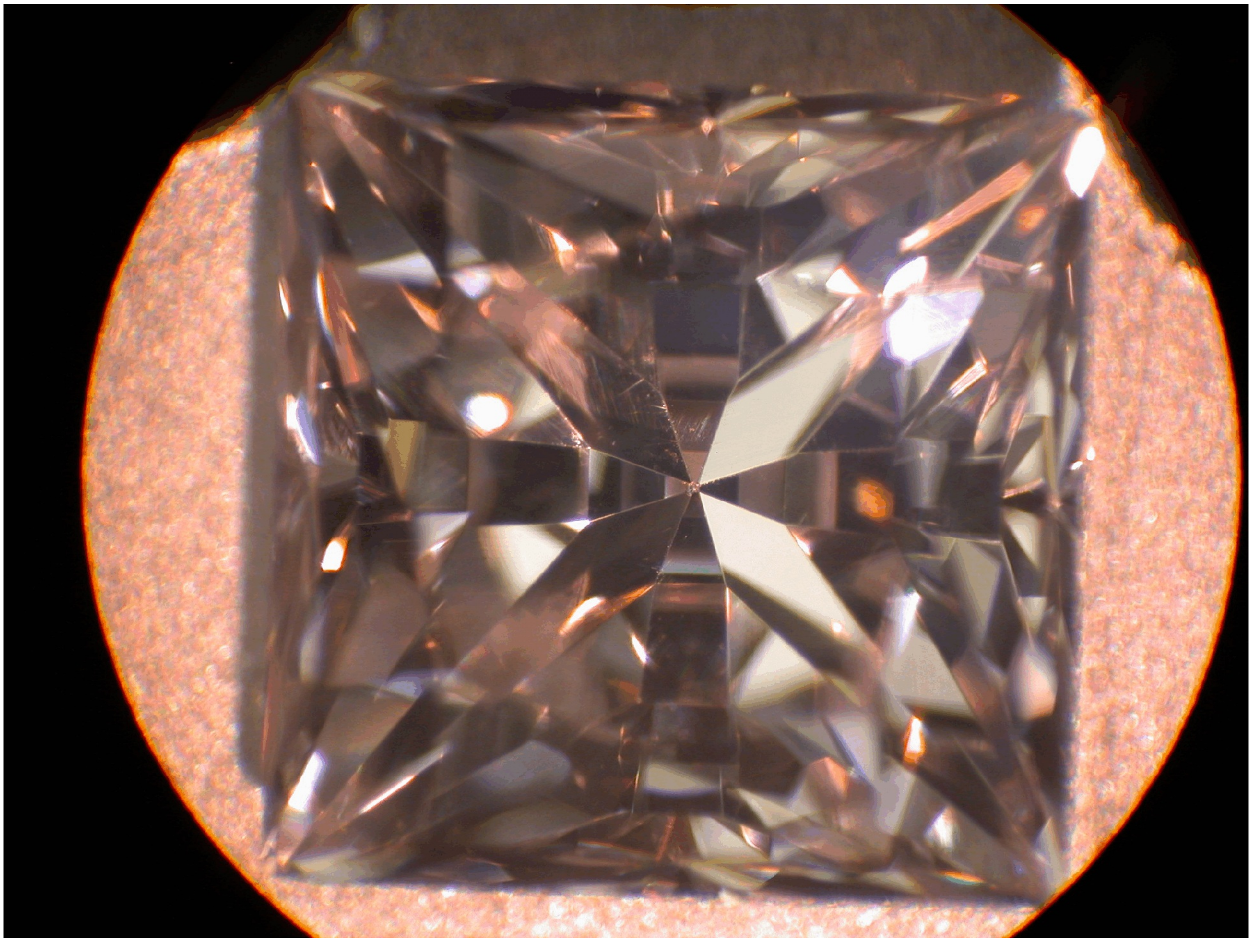

Fig. 1. The Diamond Nexus Labs 0.56 carat princess cut loose gemstone whose front face was analyzed by XPS after cleaning.

XPS Results

The surface of the front face of the Diamond Nexus Labs diamond simulant after ultrasonic cleaning and an isopropyl alcohol rinse was examined with XPS using a monochromatic aluminum x-ray source. The quantitative elemental concentration results were obtained from an elemental survey spectrum covering the binding energy range from 0 to 1100 eV with a step size of 0.5 eV and a long 4-hour data acquisition time for improved accuracy and sensitivity. The quantitative elemental concentration results for the surface are reported in Table 1.

Table 1. The elemental concentrations (in atomic %) of the front face surface of the Diamond Nexus Labs SKU GS0006 gemstone diamond simulant after cleaning:

Element	Surface after Ultrasonic Cleaning and IPA Rinse	Surface after 20s Argon Ion Sputter Cleaning, 5.6 nm Material Removal	Surface after 2nd 20s Argon Ion Sputter Cleaning, 11.3 nm Material Removal
O	48.62	56.293	57.816
C	30.34	11.703	7.242
Zr	14.27	23.245	24.915
Y	3.66	6.884	7.758
P	0.79		
Si	0.78		
Sn	0.71		
F	0.38		
Cu	0.25		
Zn	0.19		
Ar		1.875	2.269

Because of the surface sensitivity of XPS, even fairly clean surfaces will commonly have between 15 and 35% carbon on their surfaces, since hydrocarbons in the air are readily absorbed on most clean surfaces over the course of minutes. One interesting observation is that there is too much oxygen present for implied formula of

$$ZrO_2 \bullet 0.128\ Y_2O_3$$

and even assuming the Si is SiO_2, the copper either CuO, the zinc ZnO, the tin is SnO_2, ant the P is a phosphate combined with Cu, Zn, Sn, or Y there is still an excess of oxygen. This may be because ZrO_2 is susceptible to absorbing water and CO_2 to make $3ZrO_2 \bullet CO_2 \bullet H_2O$. This reaction may be the cause of the cloudiness that often times besets cubic zirconia in time. With the surface sensitivity of XPS, we may be able to observe the reaction that causes this cloudiness much earlier than it can be seen by other techniques. The amorphous diamond or diamond-like carbon coating of the Asha diamond simulant would prevent this reaction of cubic zirconia from taking place and is another advantage of its use.

On their website on the FAQs page, Diamond Nexus Labs tries to create a mystery around their diamond simulant gemstone by saying that it is a polycrystalline compound consisting of C, O, S, Fe, Co, Ni, Y, Zr, and Hf. Now, Hf is a common impurity in Zr and it is difficult to separate, but we detected no Hf in the surface. We should have seen as little as 0.02 at.%. We also did not detect S, Fe, Co, and Ni. The three transition elements Fe, Co, and Ni should have been detected if they were at concentrations of about 0.03 at.% or greater. We cannot rule out any of these "missing" elements if their concentrations are less than 0.02 at.% or at dopant levels. The claim that the gemstone is polycrystalline must come from a misunderstanding on their part. A cubic zirconia gemstone which was polycrystalline would be very undesirable and I am sure that their material is a single crystal. The polycrystalline material is good for furnace bricks, but not for gemstones, especially not given their claim to make the World's Finest Diamond-Simulant Gemstones.

Subsequently, we put this gemstone through the argon ion sputtering cleaning process in a high quality vacuum system and analyzed it with XPS in that same system. The results of the first analysis after removing only 5.6 nm of material showed that the carbon initially measured without the sputtering process was indeed just surface adsorbed hydrocarbons. This material was clearly almost entirely removed and then it adsorbed back onto the surface as we acquired the XPS data. Watching the first of many scans across the 0 to 1100 eV binding energy range that we collected the data for, no carbon was evident. I then watched this carbon concentration grow as more and more hydrocarbon was adsorbed by the cubic zirconia surface. At the end of the data collection, the carbon was measured at 11.7 at.%. Cubic zirconia surfaces have a high affinity for hydrocarbon adsorption. The formula of the cubic zirconia at this depth was approximately

$$ZrO_2 \bullet 0.148\ Y_2O_3,$$

but this does not express the very slight oxygen-deficiency at this depth. Since we do not know what part of the deficiency is with Zr and what part with Y, a more accurate formula is:

$$Zr\ Y_{0.296}\ O_{2.422},$$

which properly expresses the small oxygen deficiency with the oxygen being 0.991 times what it would be in the stoichiometric formula given above. Note that the Y to Zr ratio has increased from that on the outer surface. The argon has been embedded in the surface by the energetic sputtering. With time or mild heating this argon will desorb and disappear, since argon is inert and forms no chemical bond.

I sputtered the surface of the gemstone a second time. A total of 11.3 nm of material was now removed. These results are given in Table 1 in the last column. The carbon was again eliminated, as adsorbed surface hydrocarbons would be, and then the hydrocarbons were observed to adsorb on the face of the gemstone once again. This time, the vacuum system pressure was somewhat lower at about 3×10^{-9} Torr. At the end of the analysis, the adsorbed hydrocarbon carbon concentration was 7.2 at.%. The cubic zirconia formula at this depth was

$$\mathrm{Zr\ Y_{0.311}\ O_{2.321}}$$

A small increase in the ratio of Y to Zr has occurred with doubling the depth beneath the surface. This increase is very small compared to that from the initial surface to the 5.6 nm depth, so the ratio is already stabilizing at this small depth. The oxygen-deficiency has grown to be 0.941 times the stoichiometric concentration of oxygen, given the measured concentrations of Zr and Y. Sub-stoichiometric oxygen concentrations are fairly common in manufactured oxide materials. One reason is that the time-scale for the oxygen to react with the metal components is often rather short. Such an oxygen-deficient material will commonly have a surface which due to air contact will not be sub-stoichiometric.