CHAPTER 6

COATINGS ON GEMSTONES

The purpose of coatings is to protect dye treatments, to improve the polish by masking small scratches, grainy textures, or surface irregularities, and to stabilize porous gemstones (Hurlbut and Kammerling, 1991, p. 174-5). These treatments are used on gem material composed of more than one mineral, such as jadeite, nephrite, or lapis lazuli, to aid in polishing. Aggregate gem surfaces may be uneven and vary in hardness. Gems coated because of low hardness include alabaster, marble, rhodochrosite, soapstone, turquoise, serpentine, and amazonite feldspar. Besides low hardness, some gems are porous and the coatings keep the surface from accumulating skin oils and dirt.

Colorless coatings include waxes, paraffin, and plastics. To detect coatings, a hot needle may cause wax and paraffin to liquefy and flow, whereas plastics will have an acrid odor.

Colored Coatings and Impregnations

Colored surface coatings usually add a superficial color layer that does not penetrate the gem's surface. This enhancement can be detected with magnification if scratches, pits, or nicks appear in the coating. Some blue or purple substances have been used to treat yellowish tinted diamonds to make the stone appear more colorless. The color is usually applied to the pavilion, just below the girdle, a kind of treatment like the material used to coat or tint optical lenses. Another surface coating applied to quartz crystals is a thin layer of gold, which creates a greenish blue color with iridescence.

Colored impregnations have been employed to change white opal into black opal and to change the colors of marble and soapstone.

The application of colored tinfoil to the pavilion (back) surfaces of gemstones was common practice during the Georgian and Victorian era; this was the first treatment — aside from cutting and polishing — applied to diamond. Foiled diamonds are mounted in closed-back jewelry settings, which may make their detection problematic. Under magnification, areas where the foil has flaked or lifted away are often seen; moisture that has entered between the stone and foil will also cause degradation and uneven color.

Because of its antique status, the presence of foiled diamonds in *older* jewelry will not detract from its value

In modern times, more sophisticated surface coatings have been developed: these include violet-blue dyes (Fig. 6.1) and vacuum-sputtered films resembling the magnesium fluoride coating on camera lenses. These coatings effectively whiten the apparent color of a yellow-tinted diamond, because the two colors are complementary and act to cancel each other out (Fig. 6.2). Usually only applied to the pavilion or girdle region of a diamond, these coatings are among the hardest treatments to detect — while the dyes may be removed in hot water or alcohol with ease, the vacuum-sputtered films require a dip in sulfuric acid to remove. The films can be detected under high magnification by the presence of raised areas where air bubbles are trapped, and by worn areas where the coating has been scratched off (Fig. 6.3). These treatments are considered fraudulent unless disclosed.Another coating treatment applies a thin film of synthetic diamond to the surface of a diamond simulant. This gives the simulated diamond certain characteristics of real diamond, including higher resistance to wear and scratching, higher thermal conductivity, and lower electrical conductivity. While resistance to wear is a legitimate goal of this technique, some employ it in order to make diamond simulants more difficult to detect through conventional means, which may be fraudulent if they are attempting to represent a simulated diamond as real.

Identification of Coating in Gemtone :-Detection in loose stones can be done by boiling with acids or using a hot point or by scratching the stone with a pointed fragment. In the case of mounted stones, with the help of a lens, examine the back portion of the stone through the table. Some form of crinkling or wrinkling of the coating or foiling is visible.

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Fig. 6.1 Photograph showing coated diamond.

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Fig. 6.2 Photograph showing Coated diamond represent darker colour in front side.

Fig. 6.3 Photograph showing Coated diamond represent light colour film on backside.

This is, as described later, supposedly due to a pink layer of coating attached only to pavilion. When observing the stones immersed in methylene iodide under diffused light through a white plate, exfoliation of coating was recognised in some areas on pavilion (Fig. 6.4). Some facet edges also showed similar trace of exfoliation. Such removal of coating is hardly observed under a standard gem microscope even with specially arranged illumination, but they can be easily observed under a differential interference microscope (Fig. 6.5). Although exfoliation of coating was readily observed on all the facets on pavilion observed, coating layer was not observed on the tables and crown facets even under the differential interference microscope.

Fig. 6.4 Photograph showing exfoliation of coating in Methylene Iodide (under microscope 100X).

Fig. 6.5 Photograph showing exfoliation of coating under microscope.

Any element except carbon was not detected on the tables and crown facets by chemical analysis on the diamond surface by EDXRF. On pavilion facets Si (silicon) and Au (gold) were detected other than carbon. According to the EGL report, SiC (moissanite) was allegedly detected on the pavilion. Also GIA Insider reports that alternate layer of SiO2 and metals such as Au, Ag or Al were recognised.

Acid-resistance test using aqua regia (nitric acid 1: hydrochloric acid 3) was performed to study resistance to acid and confirm the material of the coating layer. The stone showed no change three minutes after boiling in the aqua regia. After ten minutes boiling, no change was recognised apparently, but with a differential interference microscope removal of coating layer was easily observed. Thirty minute soaking in the fluid slightly deteriorated the pink colour of the stone, and obvious exfoliation of the coating was recognised under a gemmological microscope. Then the coating layer was totally removed by rubbing the stone strongly with a jewellery cleaning cloth. The colour grade of the stone after the rubbing was K (faint brown).

High-temperature, high-pressure treatment

A small number of otherwise gem-quality stones that possess a brown body color can have their color significantly lightened or altogether removed by HTHP treatment, which was introduced by General Electric in 1999. Diamonds treated this way are all Type IIa and owe their marring color to structural defects that arose during crystal growth, known as *plastic deformations*, rather than to interstitial nitrogen impurities as is the case in most diamonds with brown color. HTHP treatment is believed to repair these deformations, and thus whiten the stone.(This is probably an incorrect conclusion, the whitening is due to destruction of stable vacancy clusters according to one of the researchers). Type Ia diamonds, which have nitrogen impurities present in clusters that do not normally affect body color, can also have their color altered by HTHP. Some synthetic diamonds have also been given HTHP treatment to alter their optical properties and thus make them harder to differentiate from natural diamonds. Pressures of up to 70,000 atmospheres and temperatures of up to 2,000°C are used in HTHP.

Also in 1999, Novatek, a Provo, UT manufacturer of industrial diamonds known for its advancements in diamond synthesis, accidentally discovered that the color of diamonds could be changed by the HTHP process. The company formed NovaDiamond, Inc. to market the process. By applying heat and pressure to natural stones, NovaDiamond could turn brown Type I diamonds light yellow, greenish yellow, or yellowish green; improve champagne Type IIA diamonds several color points, even to white; intensify the color of yellow Type I diamonds; and make some bluish grey Type I and Type IIB colorless. In 2001, however, NovaDiamond quit the HTHP gem business because of what the company's leader, David Hall, characterized as the underhanded practices of dealers. Apparently, dealers were passing off NovaDiamond enhanced gems as naturally colored, and the company refused to be party to this deception.

Definitive identification of HTHP stones is left to well-equipped gemological laboratories, where Fourier transform spectroscopy (FTIR) and Raman spectroscopy are used to analyze the visible and infrared absorption of suspect diamonds to detect characteristic absorption lines, such as those indicative of exposure to high temperatures. Indicative features seen under the microscope include: internal graining (Type IIa); partially healed feathers; a hazy appearance; black cracks surrounding inclusions; and a beaded or frosted girdle. Diamonds treated to remove their color by General Electric are given laser inscriptions on their girdles: these inscriptions read "GE POL", with "POL" standing for Pegasus Overseas Ltd, a partnered firm. It is possible to polish this inscription away, so its absence cannot be a trusted sign of natural color. Although it is permanent, HTHP treatment should be disclosed to the buyer at the time of sale.

Treated diamonds usually trade at a significant discount to untreated diamonds. This is due to several factors, including relative scarcity — a much larger number of stones can be treated to reach gem quality than are found naturally occurring in a gem quality state — and the potential impermanence of various treatments. Therefore, it is unusual to see a diamond with good overall gemological characteristics undergo treatment. Diamonds which are chosen for treatment are usually those that would be otherwise difficult to sell as gem diamonds, where inclusions or fractures noticeably detract from the beauty of the diamond to even casual observers. In these cases, the loss in value due to treating the diamond is more than overcome by the value added by mitigating obvious flaws.

Chemical vapour deposition of diamond has received a great deal of attention in the materials sciences because it allows many new applications of diamond that had previously been either too expensive to implement or too difficult to make economical. CVD diamond growth typically occurs under low pressure (10-200 torr) and involves feeding varying amounts of gases into a chamber, energizing them and providing conditions for diamond growth on the substrate. The gases always include a carbon source, and typically include hydrogen as well, though the amounts uses vary greatly depending on the type of diamond being grown. Energy sources include hot filament, microwave power, and arc discharges, among others. The energy source is intended to generate a plasma in which the gases are broken down and more complex chemistries occur. The actual chemical process for diamond growth is still under study and is complicated by the very wide variety of diamond growth processes used.

The advantages to CVD diamond growth include the ability to grow diamond over large areas, the ability to grow diamond on a substrate, and the control over the properties of the diamond produced. In the past, when high pressure high temperature (HPHT) techniques were used to produce diamond, the diamonds were typically very small free standing diamonds of varying sizes. With CVD diamond growth areas of greater than six inches diameter have been achieved and much larger area are likely to be successfully coated with diamond in the future. This is important for making many of the technologies that diamond may improve possible, and allows these technologies to be more economical to implement.

The ability to grow diamond directly on a substrate is important because it allows the addition of many of diamond's important qualities to other materials. Since diamond has the highest thermal conductivity of any material, layering diamond on to high heat producing electronics (such as optics and transistors) allows the diamond to be used as a heat sink. Diamond films are being grown on valve rings, cutting tools, and other objects that benefit from diamond's hardness and exceedingly low wear rate. In each case the diamond growth must be carefully done to achieve the necessary adhesion onto the substrate.

The most important attribute of CVD diamond growth is the ability to control the properties of the diamond produced. In the area of diamond growth the word "diamond" is used as a description of any material primarily made up of sp3 bonded carbon, and there are many different types of diamond included in this. By regulating the processing parameters-especially the gases introduced, but also including the pressure the system is operated under, the temperature of the diamond, and the method of generating plasma-many different materials that can be considered diamond can be made.

Identification of CVD diamonds

Compared to HPHT method, a reaction chamber of the device for CVD method can be enlarged easily, and this means that the method may be developed as a synthesis of lager-size diamonds. However, it is difficult for this method to grow diamond in thick layer because its growth rate is extremely low. With the technique of early 1980s, it is calculated to take four months to grow diamond layer thick enough to obtain a 0.5ct brilliant cut stone, and six months for one carat. To solve the problem of growth rate, epitaxial growth has to carry out on a {100} substrate while retaining the condition (types and concentration of source gas and temperature of a substrate) to grow {100} face in preference to {111} face (Fig. 6.6). From recent research, it is known that the growth rate can be accelerated by adding nitrogen gas, and it can achieve high speed growth rate of over 100μm/h under a good condition.

Such differences of growth environment between CVD diamond and natural diamond become key points to identify them, and the examples observed are different crystal morphology of diamonds grown in both environment and different impurity elements contained in those diamonds.

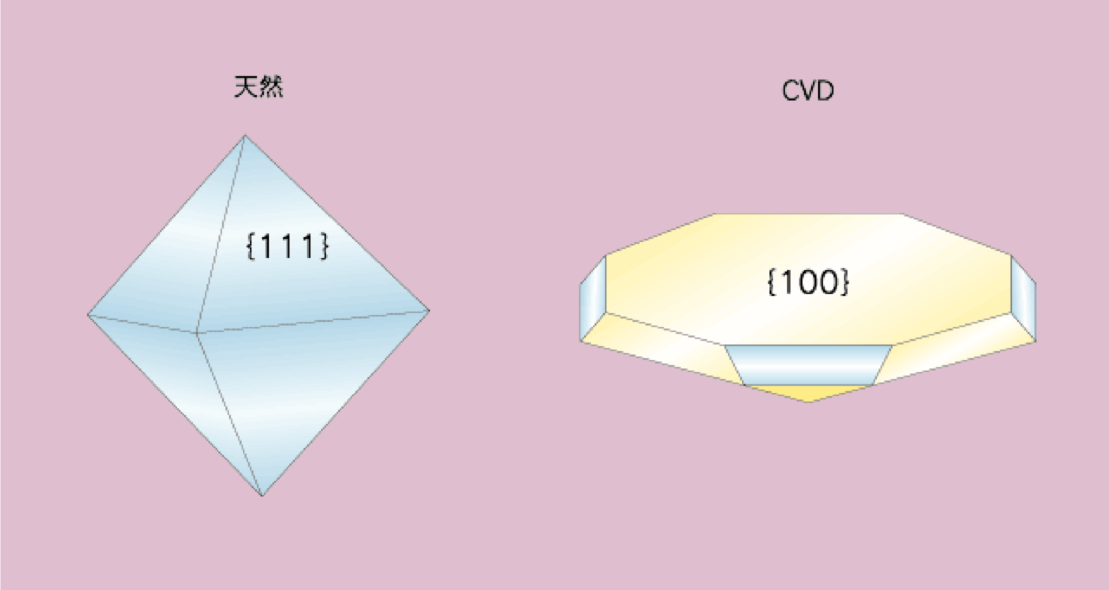

Fig. 6.6 Diagram showing morphology of natural and synthetic diamond.

CVD synthetic diamonds, which are difficult in most cases to distinguish from natural diamonds by general identification tests only. However, characteristic orange fluorescence and absence of anomalous double refraction due to strain called ‘Tatami’ structure (Fig. 6.7) that is commonly seen in type II natural diamonds are important clues for synthetic origin. Photoluminescence analysis under very low temperature may reveal some characteristic features that are not observed in natural diamonds. By Cathode Luminescence (CL) analysis, growth structure unique to CVD diamonds makes the stones positively distinguishable from natural diamonds. Application of CVD diamonds to jewellery has just started and its production is limited at the moment, but a possibility of application of CVD diamond to engineering field widely indicates further technical development. The identifying features explained in this report are based upon current products and gemmological laboratories must make efforts continuously to develop identification technique for such new material.

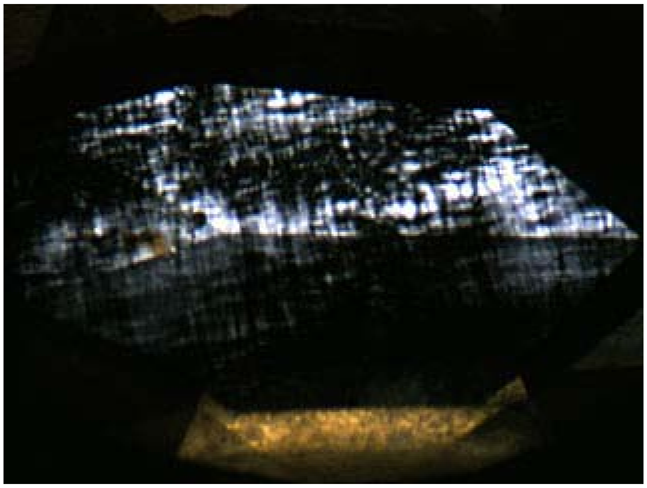

Fig.6.7 Photograph showing Tatami structure Parallel to Growth Line.

Inclusion

CVD diamonds tested this time were generally good in clarity, and two faceted pieces of Element Six were in VS class*. A few pinpoints were observed under 10X magnification in a tabular polished stone of CVD Diamond (Fig. 6.8). Further magnified observation revealed that those pinpoints were dark brown irregular-shaped substance, which is thought to be non-diamond carbon.

As CVD synthesis does not involve metal solution, metal inclusion, which is often seen in synthetic diamond produced by HPHT process, will not exist. Therefore, CVD diamond does not have magnetism, which has been announced as one of the simple identifying features for synthetic diamonds.

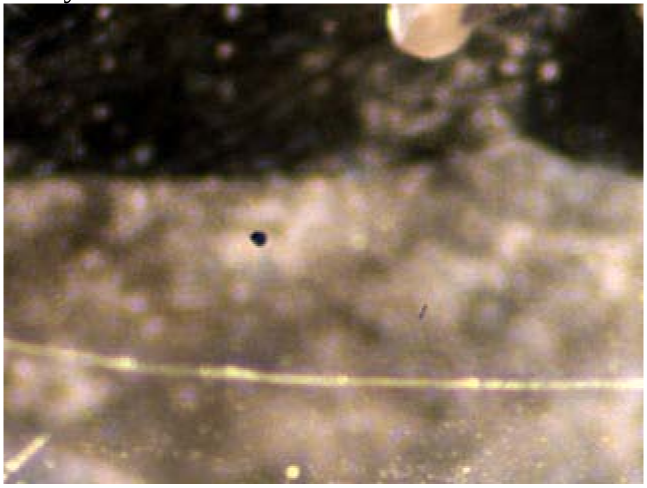

Fig. 6.8 Photograph showing a few pinpoints were observed under 10X magnification in a tabular polished stone of CVD Diamond

Colour Zoning

All CVD diamonds tested this time except one piece, which is near colourless of Element Six, have a brown hue. They are graded as Fancy Light Brown and Fancy Brown*, with a slight yellow hue. Brown colour distribution in the CVD diamonds was observed evenly throughout each stone, however some stones showed several brown lines. These are probably parallel to {100} and may have been caused by deposition of non-diamond carbon due to variation of temperature or gas pressure during its growth. Brown colour zoning seen in natural diamonds has been formed by plastic deformation that the diamond received while it reached to the earth's surface from deep under the ground where it had originally formed. It is usually observed as brown grains (planete brown colour zoning) arranged in one direction or two directions intersecting to one another.

The brown line pattern seen in CVD diamond appears not being related to anomalous double refraction due to strain that is going to be mentioned later, while the brown colour zoning seen in natural diamond is commonly associated with the anomalous double refraction showing interference colour.

UV Fluorescence

Most pieces of the CVD diamonds tested this time showed characteristic orange UV fluorescence (Fig. 6.9).

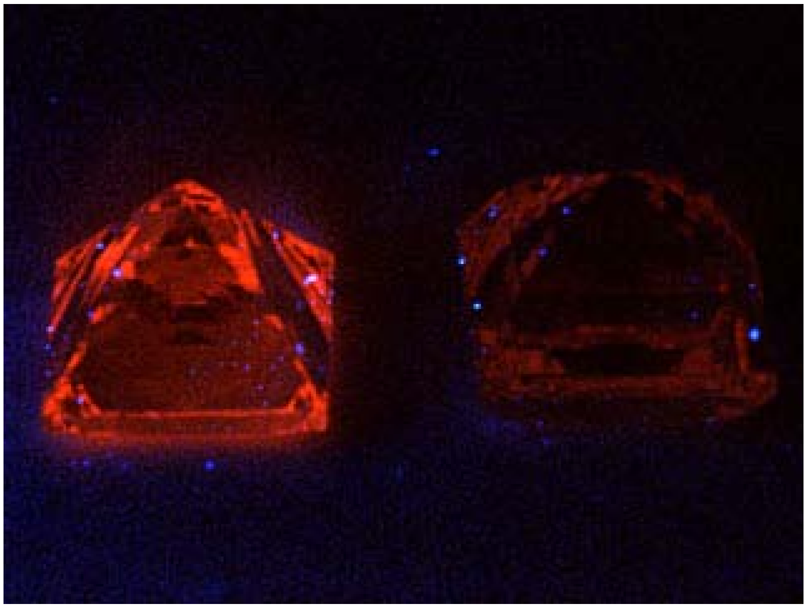

Fig. 6.9 Photograph showing orange sheen in UV Light.

They were generally more clearer in LWUV than in SWUV, but if intensity of the fluorescence is weak, it should be observed in a completely dark room. Those fluorescence colour is thought due to NV centre (575nm), which is rarely seen in a type II natural diamond. In CVD diamond, injection of nitrogen gas to accelerate growth rate and formation of void associated with generation of dislocation may be involved in production of the NV centre.