

# Surface treatment of gemstones, especially topaz – an update of recent patent literature

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**Abstract:** This review provides an overview of numerous patent documents that have been published recently and describe various coating technologies for gem materials. Parts of the documents focus on the deposition of one single or several specifically structured or composed layers in order to obtain the desired colour and the desired optical effects or wear resistance. Contact heat treatment of faceted stones with solid transition metal-bearing plates as well as heat treatment of layers deposited on the surfaces of the gemstones, are also reported. Chemical data of one sample of iron-coated topaz provide a first insight into the reaction mechanism within the outer diffusion layer.



## Introduction

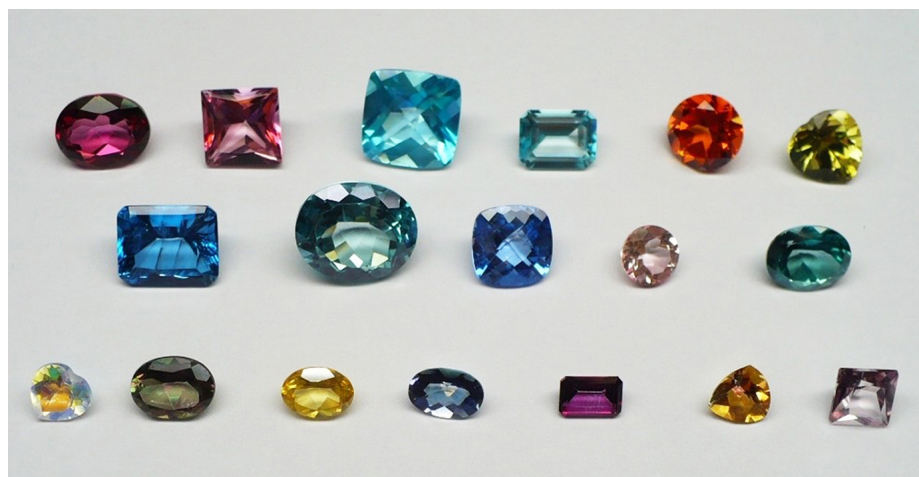
The quantity of surface-treated gem materials, especially topaz, seen in the market (*Figure 1*) is increasing. This is, at least partly, due to problems in the United States of America related to the Nuclear Regulatory Commission (NRC) rules regarding the import and distribution of irradiated blue topaz by non-licensed companies. Surface-coated topaz of various colours might, at least partly, fill the enormous demand for this relatively cheap product. Much more valuable are various other surface-treated gemstones such as coated pink diamonds; because of their value, there is a greater need to identify any treatment of such stones.

Numerous patents dealing with different types of surface treatment or surface enhancement of gemstones, especially topaz, have been reviewed and summarized by Schmetzer (2006). Four different basic technologies were reported: (a) coating with differently coloured dyes; (b) coating by chemical vapour deposition, physical vapour deposition

- or sputtering without specific heat treatment;
- (c) contact heat treatment with transition metal-bearing powder;
- (d) deposition of a coating to the faceted stone and subsequent heat treatment.

While methods (a) and (b) produce surface coatings which are easily (at least partly) removable or scratched by normal wear of the faceted stones, techniques (c) and (d) claim a more permanent surface coating. Although 'diffusion into the

*Figure 1 (above and below): Surface-coated topaz specimens treated by various techniques to obtain different colours are available nowadays from various producers. The red cushion-cut stone above weighs ??? and measures ??? × ???; the blue square-cut stone in the upper row below weighs 5.39 ct and measures 6.1 × 6.0 mm. Photos by L. Kiefert, AGTA Gemological Testing Center, New York, U.S.A.*



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outer surface' and 'chemical bonding to the surface' are described as a reaction mechanism occurring in techniques (c) and (d) which are related to heat treatment, the exact reaction mechanism or mechanisms are not known in detail. This is due to the lack of experimental data describing the chemical and/or physical properties of the surface coating layer or layers. First results have been obtained by Befi *et al.* (2006) and Kiefert *et al.* (2007), who mainly examined the chemical composition of the layer or layers nearest to the surface by X-ray fluorescence analysis (EDXRF).

Since publication of the review by Schmetzer (2006) which covered the period from about 1996 to 2005, new patent documents have been obtained and a general overview is given in *Table I*.

Detailed knowledge of possible treatment processes is essential for the recognition of treated gemstones in the laboratory, a task which becomes more and more complex for the gemmologist (see, for example, Shen *et al.*, 2007). It is a matter of speculation as to how relevant some of the matters discussed in the patents will be in the future to gemmologists, but to have outlines of such topics and to have points of reference for possible future work is, I believe, important. In addition, it should be mentioned that *Table I* summarizes only patents which are specifically related to and applied for the enhancement of gem materials and not to general surface treatments of various substances.

Some light is also shed on the importance of patents dealing with surface enhancement of gem materials if we consider the numerous law suits that occurred in the United States due to patent infringement of US patent 5,853,826 by Starcke *et al.*, issued 29 December 1998 and assigned to Azotic Coating Technology (document 3). Following the reactions of some of the companies involved, a re-examination of this patent was initiated and carried out by the United States Patent and Trademark Office (see the related re-examination communication, issued 7 May 2007). This

process led to amended claims (especially to an amended claim 1) which were published in the related 'Ex Parte Re-examination Certificate' (document 4).

### A. Deposition of a coating without specific heat treatment

#### Deposition of a coating including a wear-resistant material

A technique for the increase of wear resistance of a coloured coating is described by Neogi and Neogi (documents 17 and 18). In general, an integrated coating consisting of a colour-imparting agent and an abrasion-resistant agent is deposited on the surface of a faceted gemstone. Precursors of this technique have already been described by Nassau *et al.* (documents 1 and 2), who mentioned a diamond coating to improve and provide a harder surface on faceted moissanite that resists scratching and abrasion and by Wright (document 8), who described the coating of various gemstones by diamond-like-carbon.

In the patent applications of Neogi and Neogi (documents 17 and 18), two major embodiments are described. In one variant, the colour-imparting agent and the abrasion resistant agent are deposited in a single step within one layer. In an alternative embodiment, the colour-imparting agent is deposited in a first layer and the abrasion-resistant agent is deposited subsequently in a second layer. The colour-imparting agent may provide the perception of colour via interference phenomena or via absorption phenomena in the visible range. As examples, metals or semiconductors such as Au, Pt, Cr, Fe, Si, Ge, Bi, Ni, Co, Ta, Er, Mn, Mg, Al, Zr, Ti, Se and Be are mentioned. Furthermore, various coatings consisting of oxides, nitrides and alloys are applied. Abrasion wear resistance may be provided by integrating any of the materials such as diamond-like carbon, chemical-vapour-deposited diamond, alumina, polymer-based materials, nitrides or carbonitrides. The main example given of coated gemstones is topaz, but ruby, sapphire

and emerald are also discussed.

Sub-surface implantation methods are also described by Neogi and Neogi in documents 17 and 18 as additional possible methods to improve the appearances of gemstones. Colour can be imparted to diamonds and other gemstones via implantation of impurities using a gas cluster ion beam apparatus. Subsequent to this first step of treatment, an abrasion-resistant layer with or without an additional colour component can then be deposited on the surface of the faceted stone.

#### Deposition of a coating causing optical phenomena

A special dichroic effect is produced by a coating consisting of alternating transparent layers containing metallic and/or ceramic particles. This method is described by Gaillard Allemand in documents 15 and 16 and uses various reflection and interference phenomena. The layers are made from, for example silica, titania or magnesium fluoride and metallic chromium. A final reflecting metallic layer is deposited on these alternating layers, which may consist of titanium or chromium.

#### Deposition of a coating and formation of a diffractive optical element

Another method for the enhancement of the optical appearance of gem materials, especially for the enhancement of fire, is described by Maltezos *et al.* (documents 20 and 21). For this purpose a diffractive optical element comprising a diffraction grating is formed on one or more facets of the stone. The formation of these diffractive optical structures to enhance dispersion or fire of a gemstone, for example diamond, is performed by the deposition of that particular structure on the surface or by etching the optical structure into the surface of the gemstone. One particular technique for the formation of distinct patterns of diffractive elements is the deposition of subsequent mask and resist layers in combination with

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lithographic techniques involving various etching steps. In addition to diamond, cubic zirconia, zircon, moissanite, topaz, rutile, strontium titanate, spinel, yttrium aluminium garnet and gadolinium gallium garnet are mentioned as examples.

### B. Deposition of a coating with specific heat treatment Contact heat treatment with transition metal-bearing solids

Another group of patent publications by Rauch and Würtenberger (documents 5 to 7) describes the contact heat treatment of faceted gem materials with transition metal-bearing solids. In contrast to previous descriptions, the gem materials are not heated in transition metal-bearing powders, but in contact with a solid plate of metal or metal oxide, where, for example cobalt oxide, iron oxide or vanadium oxide form a substantial constituent of the plate. The plate has recesses in the shapes of the pavilions of the stones. The faceted gemstones, for example, corundum or topaz, are simply placed on the plate and heated for several hours in oxidizing or reducing atmospheres. The process is designed to avoid damage to the gemstones during the heat treatment process.

### Deposition of a coating to the faceted stone and subsequent heat treatment

Two groups of patent documents describe the coloration of gem materials by the deposition of colour-causing coating on the facets of the gemstones consisting of one or two layers or thin films and subsequent heat treatment.

Documents 9 to 14 by Starcke *et al.* contain descriptions of methods where heat treatment is performed preferably at temperatures below that at which substantial diffusion occurs from the coating into the gemstone. Examples are quartz, topaz and beryl. The coating applied preferably consists of two components, a carrier and a colour-causing dopant. The carrier may be any dielectric material, for example, any

metal oxide, metal nitride, metal carbide, metal sulphide or metal boride, but not a pure metal or alloy. The dopant may be a metal, alloy, oxide, nitride, boride, or another compound which is highly absorptive in the visible range. To obtain homogeneous and uniform body colours, annealing temperatures between 300 and 1150°C are given. For example, topaz can be heated at a temperature of 450°C for about one hour. It is also mentioned that the coating on the pavilion is of maximum thickness adjacent to the culet and becomes thinner with increasing distance from the culet. This type of variable layer thickness is said to improve the coloration of the gemstone.

In a recently published patent application, Yelon *et al.* (document 19) have described how to obtain a uniform colour using a coating and subsequent heat treatment technology. The coating is applied in a reactor by means of a precursor consisting of an organometallic compound, especially a metal carbonyl, or another metallic source, for example an oxide of Al, Mg or Si doped with a metal. After the deposition step the coating is typically black or metallic. If necessary, a change of colour is performed by heating in a temperature range of about 250 to 550°C in an oxidizing atmosphere. A colour change is accomplished due to the change of the valence state of the metal in the coating. Topaz, quartz, ruby, emerald, and sapphire are given as examples. Adhesion of the coating is strengthened because part of the coating material forms a diffusive layer with the gemstone substrate; topaz is given as an example.

Analytical data from this type of reaction or diffusion zone are presented by Yelon *et al.* (see again document 19). The compositional details were obtained by Auger electron spectroscopy and are given with topaz as core or substrate and iron carbonyl, Fe(CO)<sub>5</sub>, as precursor compound. The surface-related reaction or diffusion zone (*Figure 2*) consists of two sublayers. The outer sublayer with a thickness of about 50 nm contains distinct but relatively low amounts of Al and Si (from the topaz), as

well as high concentrations of iron but no fluorine. In a subsequent area, between 50 and 100 nm, the iron content decreases and the silica and alumina contents increase. It is not disclosed whether the 0–100 nm zone is in a crystalline or amorphous state. More than 100 nm from the surface, the analyses indicate that the topaz is unaffected by any diffusion. These interesting analytical results indicate that a diffusion or solid state reaction zone is formed by the heat treatment process. Its two sublayers both consist of the elements of the topaz (from the core) and iron (from the deposited metallic layer).

It is assumed that the indicated content of Fe of between 2 and 5 wt.% at 100–400 nm from the surface are iron background values attributable to the analytical technique. This is because diffusion of iron into the topaz structure to produce an almost flat profile for 300 nm is very unlikely. The data from this example therefore indicate some content of iron in the 50 nm-thick outer layer and decreasing iron contents in the 50 nm-thick inner diffusion layer, but do not support the presence of any diffused iron deeper in the crystal.

## Discussion

The patent documents reviewed in this paper and summarized in *Table 1* reflect two different basic technologies.

The first group of documents contains methods for the deposition of various thin layers or films on the surfaces of faceted stones without additional heat treatment. In documents 3 and 4 by Starcke *et al.*, 15 and 16 by Gaillard Allemend, and 20 and 21 by Maltezos *et al.*, various optical reflection and interference phenomena are used to improve the optical properties (fire) of the gemstones or to create a specific visual impression. Documents 1 and 2 by Nassau *et al.* as well as documents 8 by Wright, and 17 and 18 by Neogi and Neogi, describe the improvement of hardness and wear resistance of the gem material itself or of the colour-causing coating or layer deposited on the surface

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Table 1: Patent documents describing surface treatment of gem materials, especially topaz\*

Document/patent family**	No.	Issued	Inventor/applicant	Type of surface treatment	Coating/diffusion material	Colours (examples)	Remarks
WO 98/21386 A1	1	22.5.1998	Nassau <i>et al.</i> / C3, Morrisville, NC, USA	Chemical vapour deposition or physical vapour deposition	Diamond	Colours according to the dopant of the core	Coating of moissanite
US 5,882,786	2	16.3.1999					
US 5,853,826	3	26.12.1998	Starcke <i>et al.</i> / Azotic Coating Technology, Rochester, MN, USA	Sputtering or chemical vapour deposition or others	Thin coating of the pavilion of a stone with one or several thin layers, especially Ti, TiO <sub>2</sub> , Zr, ZrO <sub>2</sub> , also other metals, metal oxides, nitrides, sulphides and carbon	Green to violet (at different angles)	Various reflection and interference phenomena are observed when viewed at different angles of observation
US 5,853,826 C1	4	11.9.2007					
US 2003/0124299 A1	5	3.7.2003	Rauch and Württenberger/ D. Swarovski & Co., Wattens, Austria	Contact heat treatment with a solid plate	Metals or metal oxides	Blue (cobalt oxide); yellow (vanadium oxide)	Diffusion directly from the solid plate or through an additional diffusion layer between the gemstone and the solid plate
AT 411 464 B	6	26.1.2004					
US 7,033,640 B2	7	25.4.2006					
US 2003/0224167 A1	8	4.12.2003	Wright, Kirkland, WA, USA	Conventional DLC application process	Diamond-like-carbon		Improvement of optical properties and wear resistance
US 2004/0083759 A1	9	6.5.2004	Starcke <i>et al.</i> / Azotic Coating Technology, Rochester, MN, USA	Sputtering or chemical vapour deposition or others	Thin coating of the pavilion of a stone with one or several thin layers of any dielectric material, e.g. oxide, nitride, carbide, sulphide, which consists of or contains a dopant that is highly absorptive in part of the visible area	Yellow (titanium and vanadium oxide); blue (silica and cobalt oxide)	Additional heat treatment after coating is possible or necessary, but below a temperature at which diffusion from the coating into the gemstone occurs; different thickness of the coating on the pavilion with varying distance from the culet
US 6,997,014 B2	10	14.2.2006					
US 2006/0068106 A1	11	30.3.2006					
US 2006/0065016 A1	12	30.3.2006					
US 7,137,275 B2	13	21.11.2006					
US 2007/0157666 A1	14	12.7.2007					
EP 1 674 431 A1	15	28.6.2006	Gaillard Allemand/ Baccarat, Clonville, France	Various known sputtering techniques	Successive transparent layers containing metallic and/or ceramic particles with a final reflecting opaque metal layer		A decorative dichroic visual effect is produced
WO 2006/070137 A1	16	6.7.2006					

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US 2006/0182883 A1	17	17.8.2006	Neogi and Neogi/ Temecula, CA, USA	Deposition of a colour-causing material and a wear-resistant material concurrently or in two steps	Integrated coating consisting of a colour imparting agent (metal, semiconductor, oxide, nitride, alloy) and an abrasion wear-resistant agent (diamond-like carbon, CVD diamond, alumina, polymer-based materials, nitrides, carbonitrides)	Amber with secondary green effects (an integrated layer of a diamond film with chromium oxide on topaz); yellow (a diamond-like-carbon layer with Si on topaz); light green, gold and amber shades (varying levels of gold with diamond-like carbon)	The colour may be caused by bulk absorption or via interference; colour improvement by sub-surface implantation techniques and other methods are also mentioned
WO 2006/089080 A2	18	24.8.2006					
US 2007/0110924 A1	19	17.5.2007	Yelon <i>et al.</i> , Columbia, MO, USA	Chemical vapour deposition or physical vapour deposition	Organometallic compound or a metal-bearing compound as precursor for the deposition of a metallic layer	Different colours are obtainable by various precursors such as amber [Fe(CO) <sub>5</sub> ]; dark blue or green blue [Co <sub>2</sub> (CO) <sub>8</sub> ]; orange [Mn <sub>2</sub> (CO) <sub>10</sub> ]; violet [Ti(C <sub>3</sub> H <sub>7</sub> O) <sub>4</sub> ]; red [Al <sub>2</sub> O <sub>3</sub> doped with Cr]	If necessary, heat treatment of the stone with the deposited metallic layer, formation of an intermediate layer consisting of Al and Si (from the topaz core) and the metal, e.g. iron, of the precursor layer
WO 2007/067696 A1	20	14.6. 2007	Maltezos <i>et al.</i> , Fort Salonga, NY, USA	Formation of a diffractive optical element on the surface of the gemstone by deposition of a mask layer and a resist layer; lithography of the resist layer and subsequent etching	The mask layer may consist of titanium, aluminium, platinum, chromium, silicon dioxide or silicon nitride; the resist layer will depend on the lithography process and may consist of polymethylmethacrylate		The natural fire of the gemstone is increased
US 2007/0157667 A1	21	12.7.2007					

Deposition of a coating including a wear-resistant material without specific heat treatment

Deposition of a coating causing optical phenomena without specific heat treatment

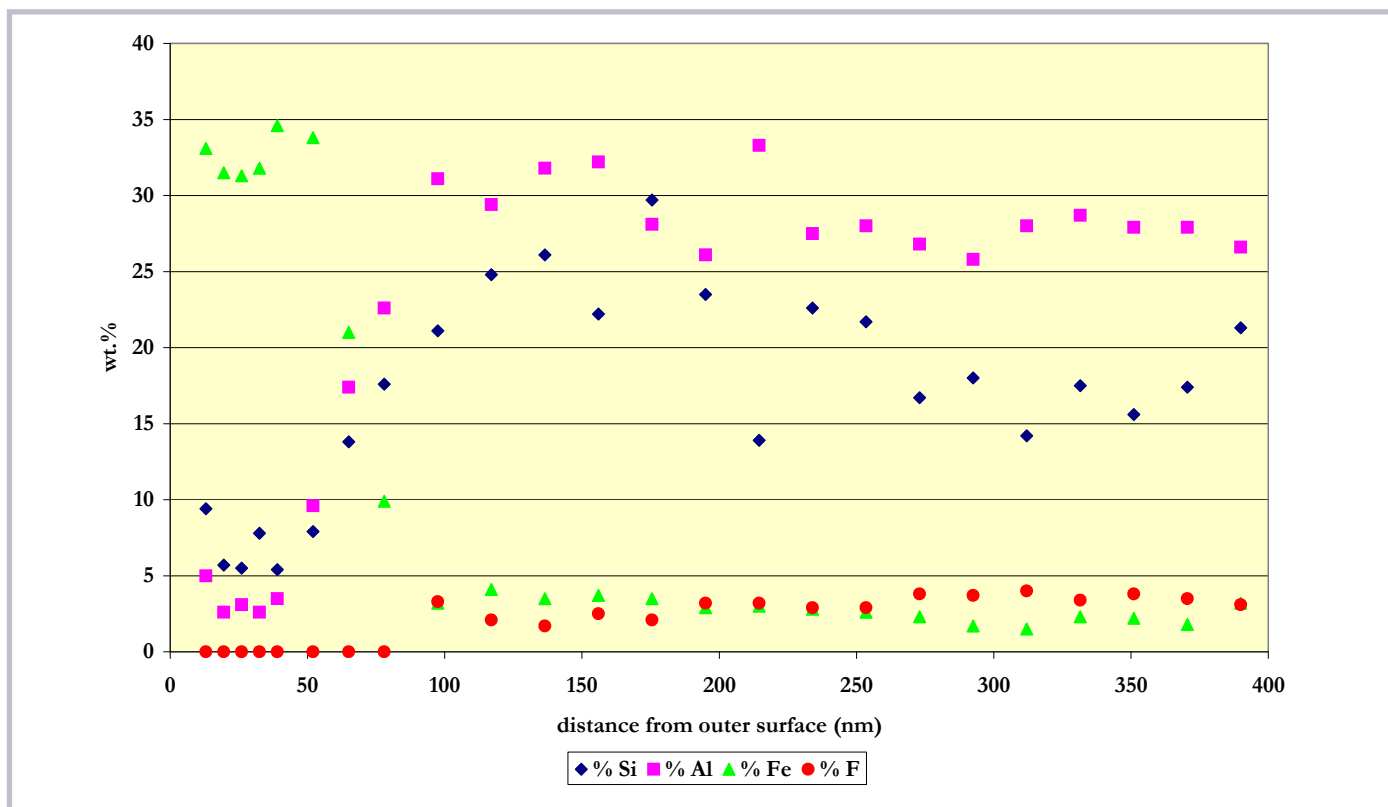
Contact heat treatment with transition metal-bearing solids

Deposition of a coating and subsequent heat treatment

\* patent documents are sorted in patent families (i.e. groups of patent documents with similar contents related to the same inventor or applicant, frequently based on the same priority application); patent families are presented chronologically according to the first member of a patent family published

\*\* Abbreviations: AT Austria; EP Europe; US United States of America; WO World Intellectual Property Organization

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**Figure 2:** Chemical zoning within the reaction and/or diffusion layer of surface-coated and subsequently heat-treated topaz. The chemical data (obtained by Auger electron spectroscopy) were taken from the patent application of Yelon *et al.* (US 2007/0110924 A1, document 19); the two outer analysis points closest to the surface were omitted because they contained artefacts of sample preparation. The diagram reveals an outer reaction zone with high iron contents (from the coating) and small but distinct aluminium and silicon values (originating from the topaz core); within an intermediate zone between this outer layer and the topaz core, an intermediate layer is observed in which the iron contents gradually decrease and the aluminium and silicon contents gradually increase.

of the gemstones. An example of this kind of material is diamond-coated synthetic moissanite which has already appeared on the gem market (Hammer and Schmetzer, 2000), and can provide misleading readings on moissanite testers.

A second group of patent publications describes techniques for the deposition of a coating accompanied by a specific heat treatment process. Documents 5 to 7 by Rauch and Würtenberger describe a new variant of the contact heat treatment technology using a solid transition metal-bearing plate as source for the colour-causing agent. For this technology previously only transition metal-bearing powders were used. Another group of patent publications consisting of documents 9 to 14 by Starcke *et al.* and of document 19 by Yelon *et al.* describes improvements of the known two-step

technology consisting of a deposition of a metal-containing layer on the surface of the gem material and subsequent heat treatment to improve or change the stability as well as the visual appearance to the coating.

Apart from surface-coated moissanite and diamond, the author is unaware of which, if any, of these various technologies has already been implemented and is in commercial production for release of such treated materials on to the market. From the descriptions given in the documents reviewed, it is very difficult to give any evaluation about the optical quality and wear resistance of the various coatings described for a number of gem materials. But it is most probable that at least some of the technologies referred to in this paper will be applied to gem materials in

the future. Consequently the recognition of these various types of treatments will be a significant focus of research for gemmological laboratories in the future.

Most interestingly, the analytical data from the margin of a topaz specimen coated with iron carbonyl (Yelon *et al.*, document 19) provides a first insight in to its chemical composition and formation as a reaction to heat treatment.

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