



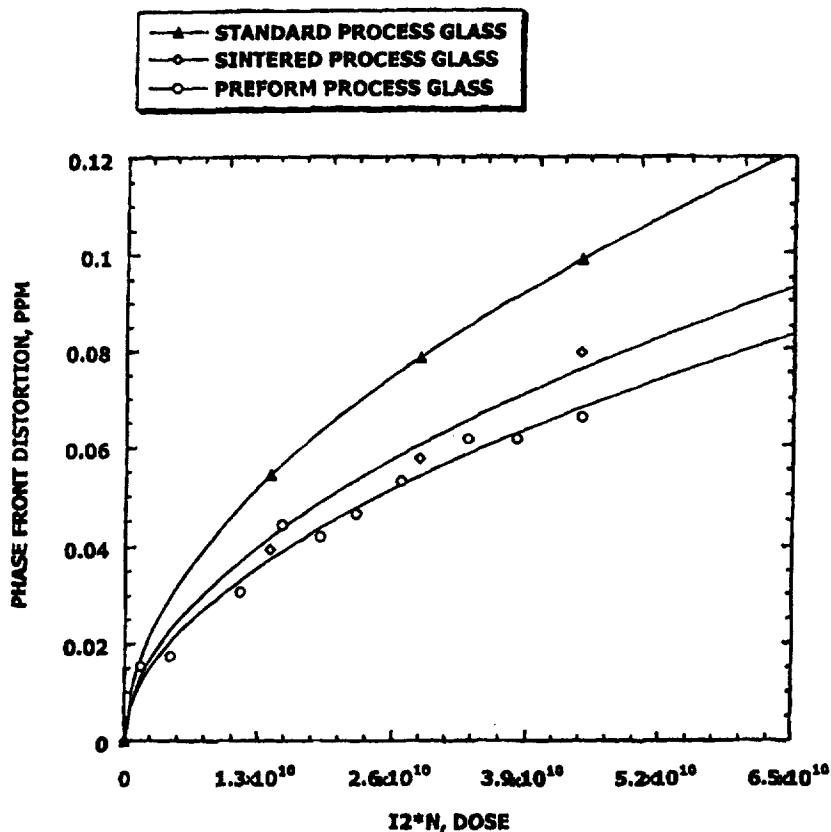
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: SILICA WITH LOW COMPACTION UNDER HIGH ENERGY IRRADIATION

## (57) Abstract

Fused silica stepper lens for photolithographic application are disclosed which are resistant to laser-induced damage, specifically, compaction or densification which can lead to an increase in the optical path length of the lens. The figure compares the phase front distortions of a standard fused silica with the phase front distortions observed in two inventive stepper lens fused silica.



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## SILICA WITH LOW COMPACTION UNDER HIGH ENERGY IRRADIATION

### FIELD OF THE INVENTION

5 This application claims priority to U.S. provisional application no. 60/024995, filed August 29, 1996. The invention relates to stepper lens from fused silica having low compaction under high energy irradiation, particularly adaptable for use in photolithography applications at wavelengths of 193 and 248 nm.

### 10 BACKGROUND OF THE INVENTION

Fused silica is highly relevant to such applications as windows and mirrors used in outer space, and increasingly, it is becoming relevant to optical elements for deep ultraviolet photolithography. However, it is generally known that prolonged exposure of fused silica to intense deep  
15 ultraviolet radiation of the type utilized in photolithography leads to optical damage which is generally manifested in the form of changes in the optical and physical properties of the glass.

20 One form of optical damage observed in fused silica glass is a physical densification or compaction of the exposed regions of the glass. Compaction is generally observed by interferometry where the alteration of the optical phase front is measured through the damaged

regions, and is reported as optical path difference, the product of refractive index and path length, in ppm or waves of 633 nm light. Thus, the optical phase front of stepper lens elements for photolithographic applications which utilize deep ultraviolet wavelengths at 193 and 248 nm for high resolution microcircuit fabrication may become altered due to optical modification as a consequence of prolonged exposure. Even though small changes in the optical phase front produced by the effect of exposure over the life of the lens barrel are expected, at present the maximum acceptable change is not known. What is known however, is that there is a relationship between alterations in fused silica and the ultimate effect of such changes on the wavefront.

The question of what factors contribute to the propensity of various silica materials to optical damage when exposed to high energy laser irradiation is not settled and several possible answers have been advanced in the literature.

Recently, in co-assigned, co-pending PCT patent application serial no. PCT/US97/11697, deposited July 1, 1997, titled "Fused Silica Having High Resistance to Optical Damage," it was suggested that radiation-caused optical damage can be minimized or eliminated by precompacting fused silica by such processes as hot isostatic pressing and by high energy pre-exposure in order to thereby desensitize the glass to subsequent high energy irradiation during actual use.

There continues to be a need for laser damage resistant fused silica. Accordingly, it is the object of the present invention to provide a fused silica stepper lens which is resistant to laser-induced damage, specifically defined as densification.

## SUMMARY OF THE INVENTION

Briefly, the invention relates to a fused silica stepper lens which is resistant to laser-induced compaction. In particular, the invention relates to stepper lenses made by flame hydrolysis, and sol gel methods.

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## BRIEF DESCRIPTION OF THE DRAWINGS

The figure compares the phase front distortions of a standard fused silica with the phase front distortions observed in two inventive stepper lens fused silica.

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## DETAILED DESCRIPTION OF THE INVENTION

Ideally, fused silica glass for photolithographic applications should be resistant to laser-induced optical damage. To be resistant to laser-induced optical damage, stepper lenses for photolithographic applications should be resistant to laser-induced absorption and compaction. However, most fused silica stepper lenses available today have shown a tendency to optically deteriorate after prolonged exposure to excimer laser radiation. We have demonstrated that stepper lenses made from fused silica glasses produced by certain processes are more resistant to laser-induced compaction than are lenses made by conventional stepper lens manufacturing methods such as the boule process.

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Structural change in fused silica has at least two ramifications: (1) a geometric change in the densified region, which gives rise to a decrease in the optical path length; and (2) an increase in the refractive index of the fused silica caused by an increase in density. These two effects result in a net change (increase) in the optical path length (optical path difference, OPD).

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Typically, density increases caused by high energy irradiation are very small (in the range of about 1 to 50 ppm), so that direct measurements of the absolute density range can be impractical. For the purpose of this work we have used interferometric measurements to characterize relative density changes across fused silica samples, measuring densified (exposed) and undensified (non-exposed) regions of each sample.

Examples of useful processes include, (1) the flame hydrolysis process described in U.S. Patents 5,043,002 and 3,933,454 both of which are sometimes referred to herein as the waveguide process; and (2) the sol-gel method described in U.S. Patent 4,789,389 which is sometimes referred to herein as the sintered process.

One method of making fused silica lenses which are resistant to laser-induced compaction is by the flame hydrolysis process. In a conventional flame hydrolysis method, a coating of flame hydrolysis-produced glass soot is deposited on a starting member to form a soot preform. The preform is consolidated to form a dense glass layer which can then be formed into a desired shape. In the consolidation step, the soot preform is subjected to a temperature in the consolidation temperature range for a time sufficient to permit the soot particles to fuse and consolidate, thereby forming a dense glass layer which is free from particle boundaries. Alternatively, such glass can be made using an improved flame hydrolysis process as described in U.S. 3,933,454. In the consolidation step of the improved process, the soot preform is heated to a temperature within the consolidation temperature range for a time sufficient to cause the soot particles to fuse and form a dense glass layer. Simultaneous with the consolidation, the glass is subjected to a stream of a substantially dry chlorine containing atmosphere.

Generally, in the fused silica process a vaporous stream of silicon-containing compound is converted, through thermal decomposition with oxidation or flame hydrolysis, to  $\text{SiO}_2$ . The gas stream is then passed into the flame of a combustion burner to form amorphous particles of fused  $\text{SiO}_2$  which are then deposited onto a support and consolidated to form fused silica. To produce the inventive stepper lens, the amorphous particles are consolidated in a chlorine-containing environment to purify the glass. In a particularly useful modified process, the deposit of amorphous particles are consolidated in a He/HCl-containing atmosphere to form a transparent glass body.

Useful silicon-containing compounds for forming fused silica glass are well known in the industry such as disclosed collectively in U.S. Patent No. 3,393,454; 4,789,389; 5,043,002; 5,152,819; and 5,154,744, all herein incorporated by reference. Preferably, the silicon-containing gaseous feedstock includes compounds that can be oxidized by flame hydrolysis or pyrolysis, to produce transparent, high-purity silica glass articles. However, for safety and environmental reasons, halide-free, cyclorosiloxane compounds are preferred.

Examples of useful halide-free silicon-containing compounds include cyclorosiloxane compounds, preferably, polymethylsiloxane such as hexamethyldisiloxane, polymethylcyclorosiloxane, and mixtures of these. Examples of particularly useful polymethylcyclorosiloxane, include, hexamethylcyclotrisiloxane, decamethylcyclopentasiloxane, octamethylcyclotetrasiloxane and mixtures of these.

In addition to polymethylsiloxanes, organosilicon materials satisfying the following three criteria can also be used to produce the inventive stepper lens:

(1) an operable organosilicon-R compound (R is an element of the Periodic Table) will have a Si-R bond dissociation energy that is no higher than that of the Si-O bond;

(2) an operable organosilicon-R compound will exhibit a significant vapor pressure at temperatures below 250°C and a boiling point no higher than 350°C; and, in the interest of safety,

(3) an operable organosilicon-R compound will, upon pyrolysis and/or hydrolysis, yield decomposition products besides SiO<sub>2</sub> which are deemed to be environmentally safe or the emissions are below acceptable governmental standards.

Three groups of compounds which have previously been found to be especially useful are categorized below according to the bonding arrangement in the basic structure:

(1) organosilicon-oxygen compounds, having a basic Si-O-Si structure, in particular linear siloxanes wherein an oxygen atom and a single element or group of elements, such as a methyl group, is bonded to the silicon atom;

(2) organosilicon-nitrogen compounds, having a basic Si-N-Si structure, such as aminosilanes, linear silazanes, and cyclosilazanes, wherein a nitrogen atom and a single element or group of elements are bonded to the silicon atom; and

(3) siloxasilazanes, having a basic Si-N-Si-O-Si structure, wherein a nitrogen atom and an oxygen atom are bonded to the silicon atom.

Other useful halide-free silicon-containing compounds for the method of the invention include octamethyltrisiloxane (an operable linear siloxane), aminosilanes such as tris(trimethylsilyl) ketenimine, linear silazanes such as nonamethyltrisilazane, cyclosilazanes such as octamethylcyclotetrasilazane, and siloxasilazanes such as hexamethyl-cyclotrisiloxazane.



In one particularly useful method of the invention, halide-free, cyclosiloxane compound such as octamethylcyclotetrasiloxane (OMCTS), represented by the chemical formula,  $---[SiO(CH_3)_2]_4---$ , is used as the feedstock in the vapor deposition processes such as used in making high purity fused silica for optical waveguide applications.

The invention is further illustrated below by reference to the figure in which the phase front distortion (ppm) is plotted versus dose of exposure,  $I^2N$ ; where  $I$  is the laser intensity, and  $N$  is the number of pulses. The reciprocity of the dose parameter allows one to calculate the total exposure dose that a sample will see without regard to the intensity or number of pulses and, using the equation given on the figure, predict the densification. What this means in the practical sense is that the quantity is what is important, not how the sample gets there.

The application for this material is photolithography, therefore, in the following sections we clearly demonstrate that the sol gel (sintered) and waveguide (preform) processes produce fused silica glasses which are less compacting over the predicted lifetime of a lithographic lens than fused silica lenses made by the standard (boule) process. In the figure, the result for the fused silica sample produced from the standard boule process is represented by triangles, the sintered process by diamonds, and the preform process by circles. Sample geometries and laser exposure arrangements were the same for all samples studied.

The plotted phase front distortion for the sintered process was obtained directly from interferometric data. For the preform process, the peak-to-valley phase front distortion was calculated from birefringence measurements using the conversion reported in Borrelli, Smith, Allan, and Seward, "Densification of fused silica under 193-nm excitation", J. Opt. Soc. Am. B/Vol. 14, No. 7/July 1997, 1606, and Allan, Smith, Borrelli, and Seward, "193-nm excimer-laser-induced densification

of fused silica", OPTICS LETTERS/Vol. 21, No. 24/ December 15, 1996, 1960, incorporated herein by reference. For the standard fused silica glass we used samples of Corning's Code HPFS® fused silica (Corning, New York), which had been optimized for deep ultraviolet transmittance and optical homogeneity.

In the figure we have shown data from 0 to about 0.4 (633nm) waves, which is reasonably the practical limits of distortion for photolithographic application. The figure compares the measured compaction between fused silica made by the standard process (triangles) glass and stepper lens fused silica made by the sintered (diamonds) and waveguide (open circles) processes over the lifetime of a lens. For this purpose, we have assumed that the optical elements will be subjected to a fluence ( $I \cdot t$ ) of 0.5 mJ/cm<sup>2</sup>/pulse for 8 years. We have further assumed that the laser will have a repetition rate of 1000Hz and the stepper containing the lens will be run for 7 days a week, 24 hours a day, 365 days a year, yielding a lifetime dose ( $I^2N$ ) of 6.3x10<sup>10</sup>. Inspection of the graph shows that fused silica made by the standard process exhibits about 0.28 waves of distortion at this dose, while fused silica made by the sintered and waveguide processes exhibit phase front distortions of only 0.22 and 0.18 waves, respectively. It is significant to note that the curves for the sintered and waveguide samples are below the curve for the standard process glass over the entire lifetime of the fused silica.

It is to be understood that various changes and modifications which do not constitute departures from the spirit and scope of the invention will be apparent to persons skilled in the art, which changes and modifications are embraced by the present invention.

## CLAIMS:

1. Stepper lens made from fused silica glass which is resistant to compaction when exposed to a dose of high intensity excimer radiation.

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2. Fused silica stepper lens which is resistant to compaction when exposed to high intensity excimer radiation, said lens being made by a process comprising the steps of:

(a) preparing a solution which contains at least one silicon-containing organic compound having the formula  $\text{Si}(\text{OR})_4$  or  $\text{SiR}(\text{OR})_3$ , where R is an alkyl group;

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(b) polymerizing the silicon in the solution to form a  $\text{SiO}_2$  gel;

(c) drying the gel at a rate which causes the gel to fragment into granules having a mean particle size less than about one millimeter;

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(d) sintering the granules at a temperature less than about  $1150^\circ\text{C}$ , the density of the granules after sintering being approximately equal to their maximum theoretical density;

(e) forming a green body from the sintered granules;

(f) drying and partially sintering the green body in a chamber by (i) raising the temperature of the chamber to above about  $1000^\circ\text{C}$ , and (ii) introducing chlorine gas into the chamber and/or subjecting the chamber to a vacuum and/or purging the chamber with an inert gas; and

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(g) fully sintering the green body in a chamber by raising the temperature of the chamber to a temperature above about  $1720^\circ\text{C}$ , while purging the chamber with helium or applying a vacuum to the chamber.

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3. Stepper lens according to claim 2 wherein the process includes the additional step after step (g) of hot isostatic pressing the fully sintered green body to a chamber by raising the temperature of the chamber to above about 1150°C and introducing an inert gas into the chamber at a pressure above about 100 psig.

4. Stepper lens according to claim 2 wherein the solution of step (a) contains tetraethylorthosilicate having the formula  $\text{Si}(\text{OC}_2\text{H}_5)_4$

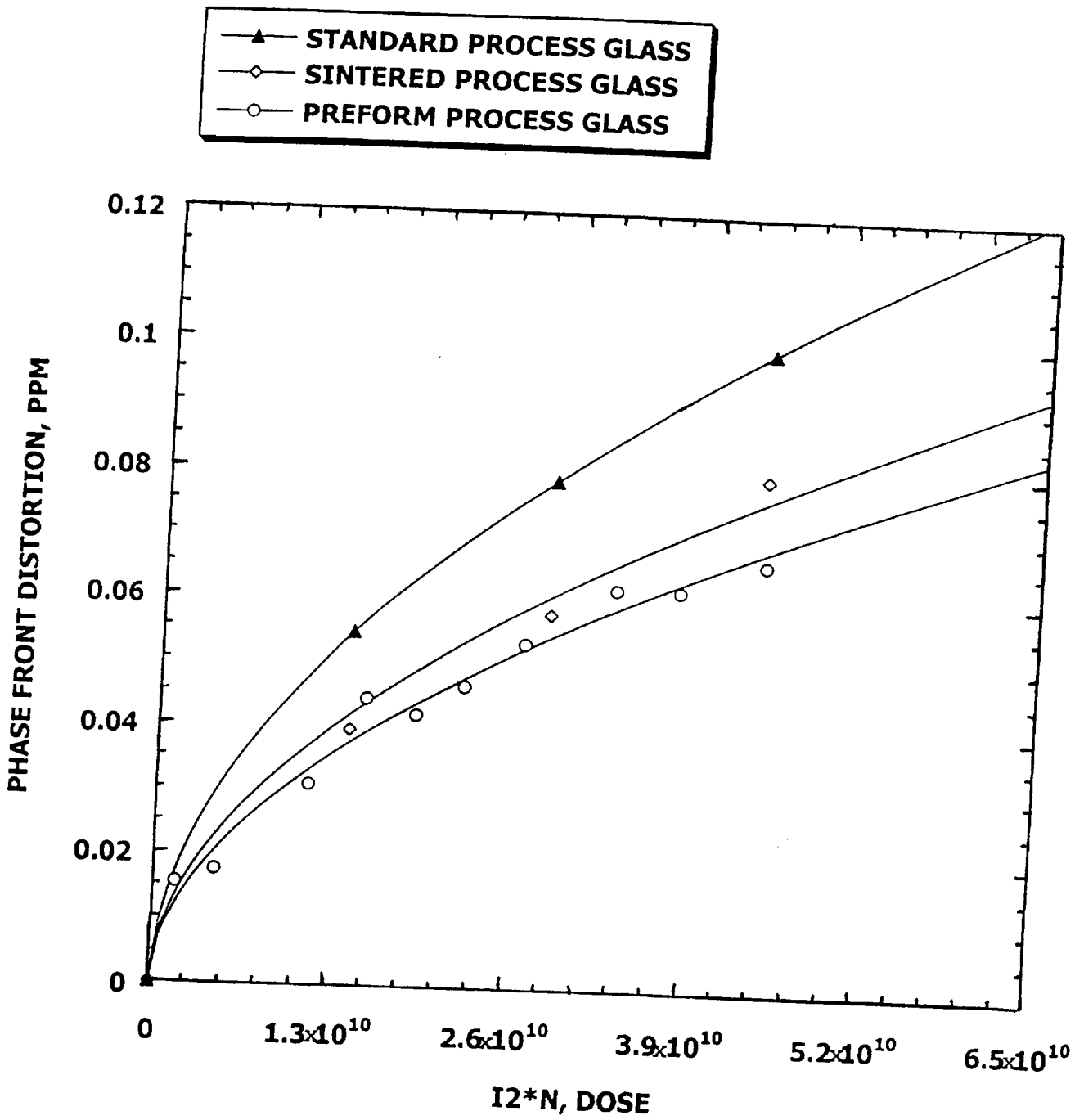
5. Fused silica stepper lens which is resistant to compaction when exposed to high intensity excimer radiation, said lens being made by a process comprising the steps of:

(a) depositing on a starting member a coating of flame hydrolysis-produced glass soot to form a soot preform;

(b) consolidating the soot preform to form a dense glass layer free from particle boundaries; and

(c) forming said dense glass layer into a stepper lens;

said consolidation step being characterized in that it comprises heating said soot preform to a temperature within the consolidation temperature range for a time sufficient to cause said soot particles to fuse and form a dense glass layer, and simultaneously subjecting the soot preform to a stream of a substantially dry, hydrogen-free, chlorine containing atmosphere.



# INTERNATIONAL SEARCH REPORT

Inte...ational application No.  
PCT/US97/15233

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : Please See Extra Sheet.

US CL : 501/54,12,900; 65/17.2,17.4

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 501/54,12,900; 65/17.2,17.4

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,364,433 A (NISHIMURA et al) 15 November 1994, col. 4, lines 3-15 and col. 9, lines 55-60.	1, 5
Y	US 5,523,266 A (NISHIMURA et al) 4 June 1996, col. 6, lines 1-10 and col. 9, lines 31-33.	1 and 5
Y	US 4,789,389 A (SCHERMERHORN et al) 6 December 1988, col. 3, line 60-col. 4, line 29, col. 6, lines 20-24 and col. 5, lines 50-55.	1-4
Y	US 3,933,454 A (DELUCA) 20 January 1976, col. 4, line 57-col. 7, line 39 and claim 1.	1 and 5
Y	US 5,043,002 A (DOBBINS et al) 27 August 1991, examples.	1 and 5

Further documents are listed in the continuation of Box C.       See patent family annex.

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Date of the actual completion of the international search <p style="text-align: center;">17 NOVEMBER 1997</p>	Date of mailing of the international search report <p style="text-align: center; font-size: 1.2em; font-weight: bold;">10 FEB 1998</p>
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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/15233

## A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

C03C 3/6; C03B 8/02,04