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Suehiro TAKEUCHI and Eiko TAKEKOSHI

日本原子力研究所
Japan Atomic Energy Research Institute

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Surface Treatment of Glass Substrates for the Preparation of Long-lived Carbon Stripper Foils

Suehiro TAKEUCHI and Eiko TAKEKOSHI
Division of Physics, Tokai Research Establishment, JAERI

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Glass substrates having uniformly distributed microscopic grains on the surfaces are useful to make long-lived carbon stripper foils for heavy ions. A method of surface treatment of glass substrates to form the surface structure is described. This method consists of precipitation of glass components, such as soda, onto the surfaces in a hot and humid atmosphere and a fogging treatment of forming microscopic grains of the precipitated substances. Some results of studies on the treatment conditions are also presented.

Keywords: Surface Treatment, Glass Substrates, Long-lived Carbon Stripper Foils, Precipitation Treatment, Fogging Treatment

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長寿命荷電変換炭素薄膜を製作するためのガラス基板の表面処理

日本原子力研究所東海研究所物理部
竹内　末広・竹腰　英子

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重イオンビーム用荷電変換膜として，寿命の長い炭素薄膜を製作するには，蒸着用ガラス基板としてその表面上に膜厚程度の大きさの微粒子が一様に分布したものを使用すると有効である。この表面状態を形成するために開発したガラス基板の表面処理法について述べる。この方法は，ガラスを高温高湿度の雰囲気中に入れておくとガラス中のソーダ等の成分がガラス表面に析出する現象，およびその表面を水蒸気で曇らせると析出物が一様に粒状化する現象を利用している。処理条件に関する試験結果もまた提示されている。

Contents

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1. Introduction

Acceleration of heavy ions in tandem accelerators needs long-lived carbon stripper foils, while a thin self-supporting carbon foil usually available shrinks under bombardment with heavy ions and ruptures in a short period. There have been many works to improve the lifetime and some success-full improvements in the lifetime[1,2,3]. Glass substrates treated by using a weathering phenomenon of glass surfaces have been found to be effective to produce long-lived foils, by S. Takeuchi et al[1]. They reported that their foils of 10 $\mu g/cm^2$ in thickness and 10 mm in diameter had lifetimes of 5 to 10 hours under the bombardment of 3.5 MeV Ar^+ beams with the intensity of 1 $\mu A/13mm^2$, while usual foils had lifetimes of only 10 to 30 minutes under the same bombarding condition.

Their preparation method is characterized by the following four points: 1) use of carbon DC arc-discharge as the evaporation source, 2) use of nickel chloride as the releasing agent, 3) use of glass substrates of which surfaces are fogged with fine grains of precipitated substances and 4) heating of the substrates. Among them, the use of fogged glass substrates had an effect of making the lifetimes 3 to 6 times longer. The appropriate surface structure was characterized by a uniform distribution of grains with the size of the same order as the foil thickness or 0.05 to 0.1 μm and the density of 2 to 3 $\times 10^5$ grains/mm^2. The fogged surface structure was copied to the carbon foils as a replica in the deposition process. Under the Ar^+ beam bombardment, the replica structure was effective to release the tension induced by the shrinkage of the irradiated area because of its stretching capability. A remarkable stretch was observed at the periphery of the irradiated area.

This paper is concentrated on the description of the treatment procedure of glass substrates to form the appropriate grain distribution. The main feature of this treatment is a kind of weathering of glass surfaces in a hot and humid atmosphere. The weathering phenomenon is described in section 2 and the preparation procedure of the substrates is in section 3. Some results of examinations of treatment conditions are presented in section 4.

2. Weathering Phenomenon in Glass

Slides of soda glass for photomicroscopy are convenient for substrates in thin film deposition. Such a glass possessing low chemical durability is rapidly weathered to have a heterogeneous surface layer in a hot and humid atmosphere[4,5]; a component of glass, such as sodium oxide, diffuses out to

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Slides of soda glass for photomicroscopy are convenient for substrates in thin film deposition. Such a glass possessing low chemical durability is rapidly weathered to have a heterogeneous surface layer in a hot and humid atmosphere[4,5]; a component of glass, such as sodium oxide, diffuses out to the surfaces because of mobility enhancement due to heat and reacts with water vapour as follows[4,6],

$$Na_2O \quad + \quad H_2O \quad \longrightarrow \quad 2\ NaOH$$

The sodium hydroxide later reacts with CO_2 in the air to form sodium carbonnate. When acid vapour is contained in the atmosphere, it neutralizes the sodium hydroxide to form salt. Similar reactions may happen to other components of glass if they possess enough mobility. The precipitation of such components onto the surfaces makes the inner surface layer silica rich[4], as is schematically shown in Fig. 1-a.

In the present treatment procedure, glass surfaces are attacked with hydrochloric acid vapour after the precipitation treatment, so that the surfaces are covered with a thin layer of salts, such as sodium chloride. The surfaces are fogged by exposing to wet steam and the salt layer becomes granulated because of coaguration in the drying process, as is schematically shown in Fig. 1-b.

3. Preparation Procedure

The preparation procedure of the glass substrates consists of cleaning of glass slides, precipitation in a constant temperature/constant humidity cabinet and fogging treatment of the glass surfaces.

The glass slides used here were colorless soda-glass slides manufactured by Matsunami Glass Industries, Ltd., Japan (catalogue number S1111). The approximate composition is 68% SiO_2, 10.5% Na_2O, 3.5% K_2O, 13% alkaline-earths and 2.5% Al_2O_3 in weight percent. The treatment procedure described below is believed to be applicable to other soda-glass slides possessing different compositions with a minor change of treatment conditions.

a. The cleaning procedure is as follows:

(1) A precleaning with synthetic detergent.

(2) A ten-minute cleaning with 2% hydrochloric acid at 50°C.

(3) Rinse in distilled water.

(4) A boiling in distilled water, followed by rapid drying.

Fresh glass slides should be used because old ones may have cracks on the surfaces and may be weathered already. In process (1), glass slides are rubbed with fingers so as not to make scratches on the surfaces. Process (2) is a mild etch of the surfaces. The aim of process (4) is a rapid drying to prevent dust in the air from depositing onto the surfaces. Alcohol or ether can be used instead of distilled water.

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b. Precipitation and fogging treatments:

(1) Storage for 18 hours in a constant temperature/constant humidity cabinet, in which the temperature is 70°C and the relative humidity is 80%, followed by cooling down and drying up to the room conditions.

(2) Exposure for 5 minutes to the atmosphere containing 1% hydrochloric acid vapour at room temperature.

(3) Exposure to almost saturated water vapour of 40°C for 2 to 5 seconds.

The growth of the precipitates on a glass surface depends on storage time, temperature and humidity. The storage time necessary for the preparation of fogged glass substrates is 1 to 2 days for 60°C, 12 to 24 hours for 70°C or 1 to 3 hours for 80°C in the use of glass slides Matsunami S1111. The relative humidity is desired to be higher than 60%. It may be necessary to change the storage time or the temperature in use of other kind of glass.

The precipitated alkali is neutralized in process (2). For producing hydrochloric acid vapour in a chamber, it is convenient to pour a drop of hydrochloric acid into a cup of concentrated sulfuric acid. The atmosphere in the chamber must be dry before the vapour generation in order to avoid a generation of heavy mist which might sprinkle over the glass slides.

In process (3) for the fogging treatment, the exposure time is determined by observing a sample slide through a dark-field photomicroscope. Desirable grain density and size are 2 to 3 $\times 10^5$ grains/mm^2 and 0.05 to 0.1 μm, respectively, from the result of the lifetime experiments of the carbon foils using Ar^+ beams[1).

4. Studies for the Optimum Conditions

In order to get the optimum grain size and density, we have examined the dependence on the conditions; temperature, humidity and storage time in the precipitation treatment and exposure time in the fogging treatment. The experimental procedure was as follows. A set of glass slides (Matsunami S1111) cleaned according to the cleaning procedure a. in section 3 was kept in a constant temperature/constant humidity cabinet, exposed to 1% hydrochloric acid vapour in a 50-liter chamber for 5 minutes and fogged with 40°C water vapour for an exposure time of 1 to 10 seconds. The 5-minute exposure to the hydrochloric acid vapour was enough to neutralize precipitated alkali. The water vapour was maintained to be nearly saturated by warming water in a

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3-liter beaker covered with a lid which had a hole for putting a slide in and out. The glass surface was observed through a dark-field photomicroscope.† The room temperature during the fogging treatment and the surface observation was between 20°C and 22°C.

The followings are the results taken with the precipitation temperature of 70°C and the storage time of 18 hours. Figure 2 shows that the distribution of grains becomes sparse with the fogging exposure time. The grain size naturally becomes greater as the density decreases. Figure 3 shows the dependence of the density on the exposure time at different five relative humidities of 13% to 80%. Figure 4 shows a similar dependence in the case of repeating a short time exposure, where the density changes slowly with the repitition times.

The density apparently increases with the relative humidity and is saturated at about 60%. Relative humidity of 60% to 80% is appropriate for the preparation of fogged glass substrates, where high grain density can be obtained with less humidity dependence. An appropriate exposure time to form the density of 2 to 3 $\times 10^5$ grains/mm^2 and the size of 0.05 to 0.1 μm lies between 2 and 5 seconds for the precipitation conditions of 70°C and relative humidity of 60% to 80%.

On the other hand, the precipitation rate increases with the precipitaion temperature because of mobility increase of glass components. Figure 5 shows the dark-field photomicrograghs of the glass surfaces which were stored for 18 hours at 50°C, 60°C, 70°C and 80°C for precipitation. Temperatures 60°C to 70°C yielded proper grain distribution for the storage time of 18 hours. A more wider survey on the storage time and precipitation temperature resulted in the optimum conditions of 1 to 2 days for 60°C, 12 to 24 hours for 70°C and 1 to 3 hours for 80°C

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†Nikon Metaphot Model VMD with object lenses of 100× and 40× and eyepieces of 10×.

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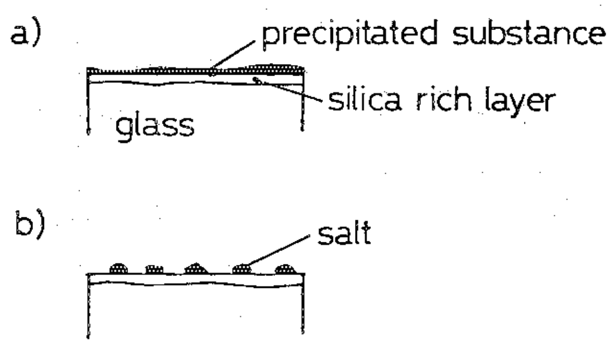

Fig. 1 Schematic sketches of a) heterogeneous layer on glass surface weathered in a hot and humid atmosphere and b) surface structure after a fogging treatment.

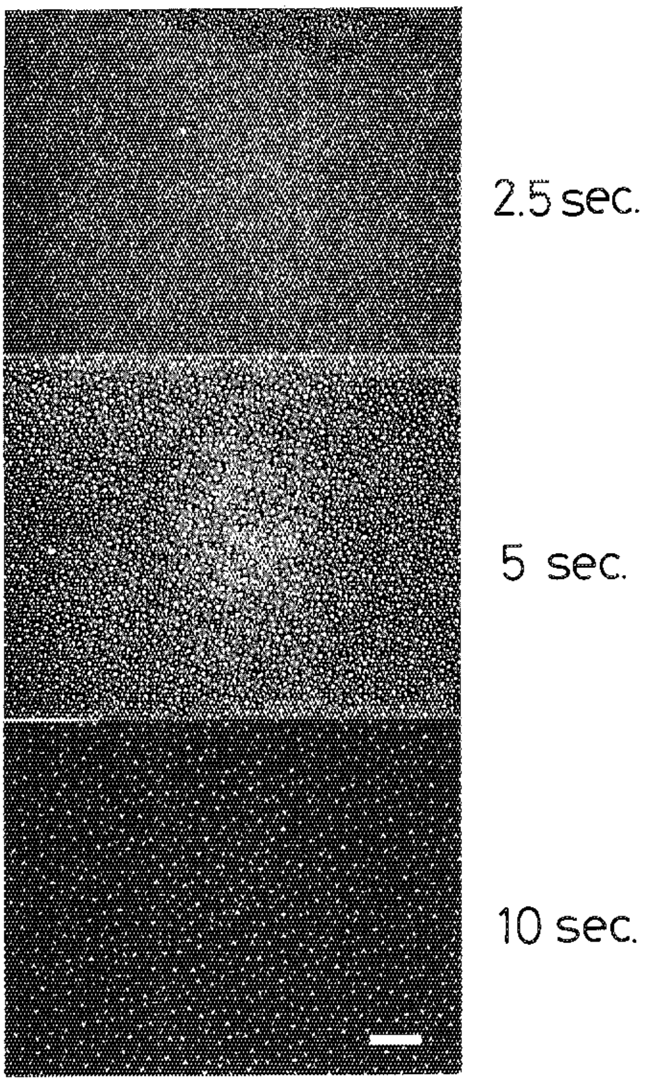

Fig. 2 Dark-field photomicrographs of glass surfaces fogged with different exposure times of 2.5, 5 and 10 seconds after 18 hour precipitation at 70°C and relative humidity of 60%. White bar is 20 μm in length.

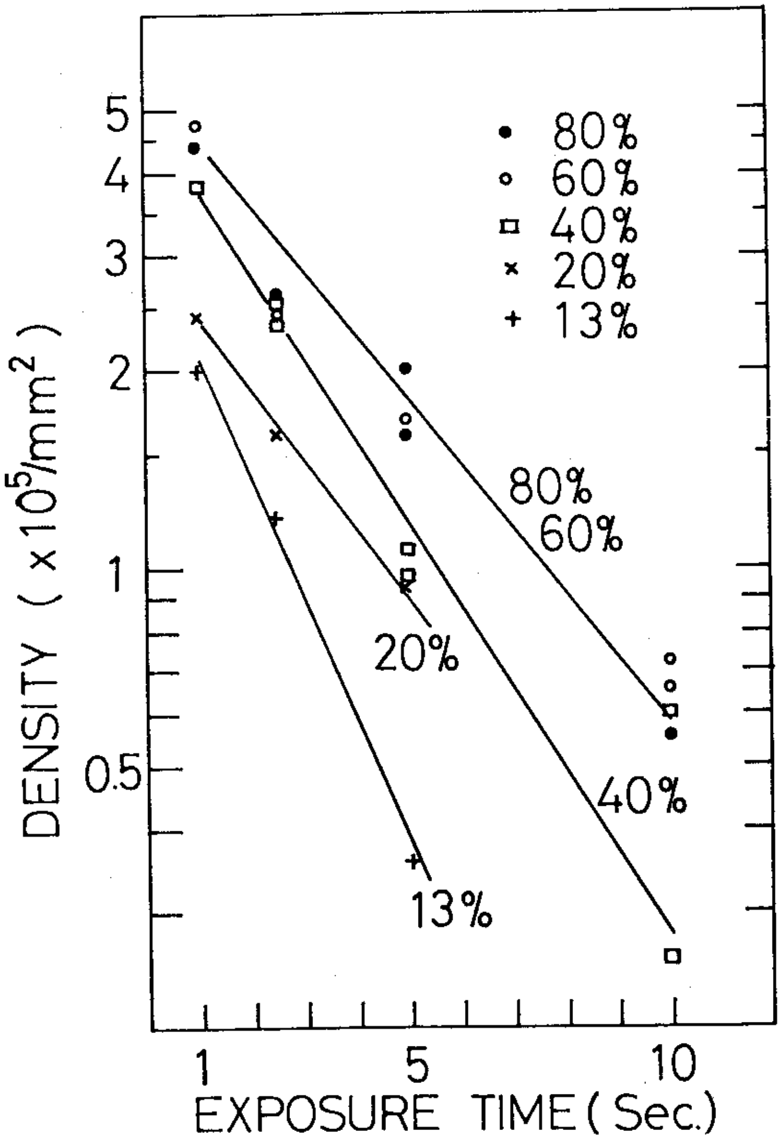

Fig. 3 Grain density curves as a function of fogging exposure time. The glass slides were treated for 18 hours at precipitation conditions of 70°C and relative humidities of 13% to 80%. Lines are drawn to guide the eye.

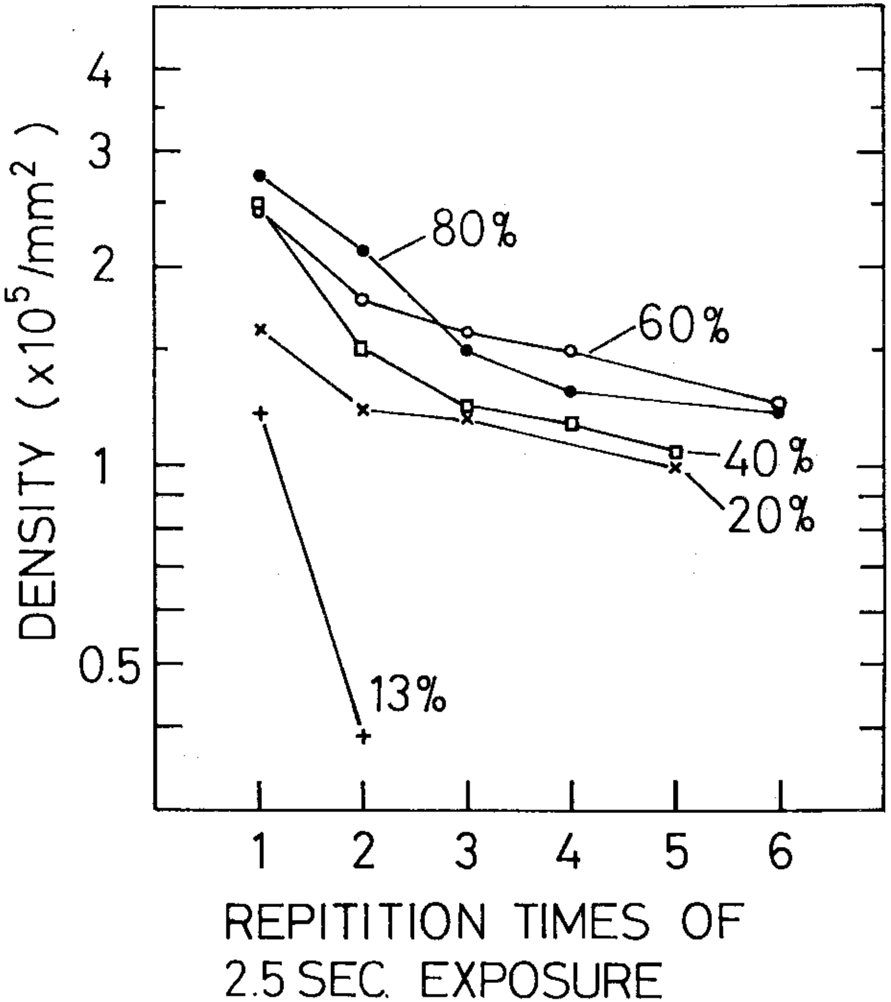

Fig. 4 Grain density curves as a function of repitition times of fogging exposure. The glass slides were treated for 18 hours at precipitation conditions of 70°C and relative humidities of 13% to 80%. The exposure time for each fogging is 2.5 seconds. Lines are drawn to guide the eye.

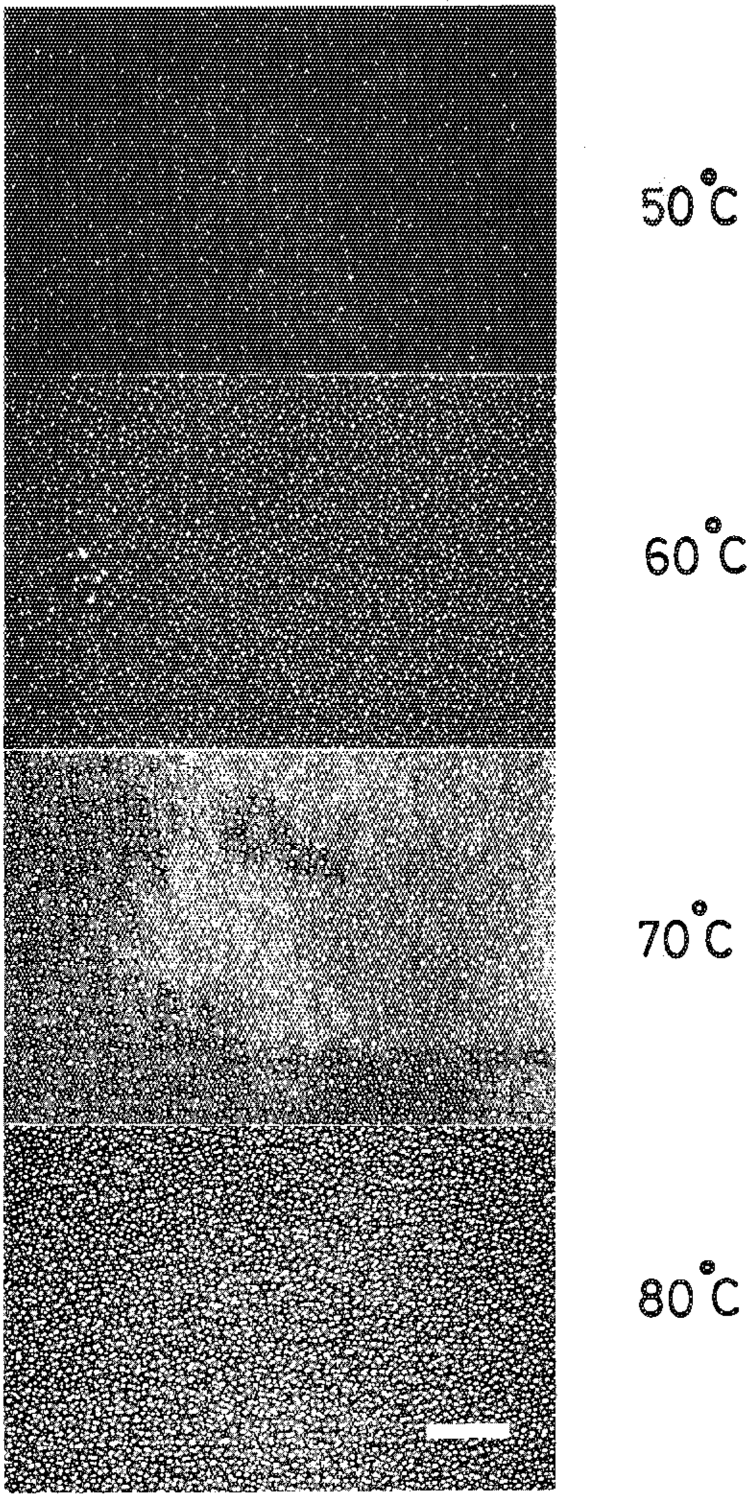

Fig. 5 Dark-field photomicrographs of glass surfaces fogged after the precipitation at 50°C, 60°C, 70°C and 80°C. The relative humidity in the precipitation is 80%. The fogging exposure time is 2.5 seconds. White bar is 20 μm in length.