

Abstract

We present source design and process results of a linearly scalable ribbon ion beam for modifying glass surfaces by an ion implantation technique. Our source technology enables beam currents up to 30 mA/cm^2 and ion implant energies up to 60 keV enabling economically viable large format and high throughput processing. In this paper, we demonstrate application of this ion source towards the production of glass and sapphire substrates with durable broadband anti-reflection surfaces with reflectance $<0.5\%$ in the visible spectra. In addition, the anti-reflection surface is shown to remain after subsequent tempering and chemical strengthening processes.

Key Words

ion implantation, anti-reflection, surface modification, display glass, large format substrates, automotive

Technical Summary

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Objective and Background:

Our team has developed a linearly scalable ribbon beam for industrial scale ion implantation processing of large format substrates.¹ The source is capable of producing beam currents up to 30 mA/cm^2 and ion energies up to 60 keV enabling economically viable high throughput processing for various surface modification applications. In particular, we show that we can produce a graded index optical layer in the surface of glass and sapphire substrates resulting in surface reflectance of $<0.5\%$ in the visible and NIR spectral range. In addition, this surface modification technique is shown to be robust and capable of surviving both glass tempering and chemical strengthening processes making the application particularly well suited for production of outdoor display, automotive, solar, and other substrate types used in physically demanding environments. Images of the source are included in Figure 1.

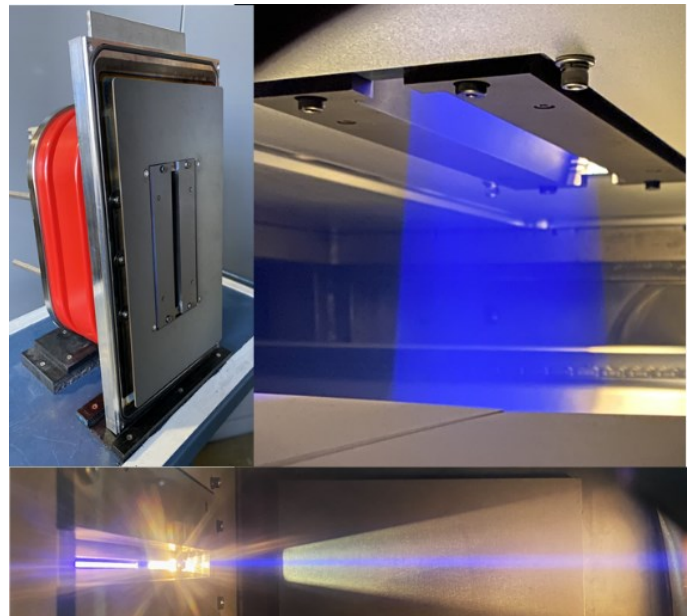


Figure 1. Images of 200mm ion source ready for installation into the plasma processing system (upper left) and during operation (upper right). Images show the well-controlled beam divergence capable (bottom)

The patented source design² couples the features of a standard Bernas-White source with an innovative quadrupole cusping field magnetic structure to achieve linear scalability substantially independent from the uniformity of the magnetic field. A tungsten filament provides electrons through thermionic emission; a triode design provides ion extraction, suppression, and ground electrodes for generating a neutral space-charged beam with controllable beam divergence. The single slit architecture enables high ion fluxes and simple electrode alignment. Magnetic confinement within the source body allows for electrons to traverse the length of the source many times prior to returning to the anodes, enabling uniform plasma generation and enabling beam lengths of virtually any arbitrary length. A schematic of the source cross-section is provided in Figure 2.

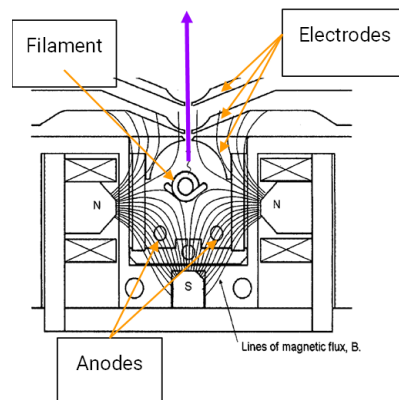


Figure 2. Cross-section schematic of source design. Taken from Ref. 1

The source can output up to 1 amp of ion current per linear meter or up to 30 mA/cm² with ion energies ranging from 100eV up to 60keV. The beam produces a narrow range of ion energy outputs enabling precise and tailored ion energy control. To demonstrate this, a faraday cup with retarding grid was placed in the beam path and the ion energy was measured. Figure 3 demonstrates the ion energy output produced for several different voltages. This contrasts with the only other scalable linear ion source, the closed drift anode layer design, which produces a much broader range of ion energies. These data were generated using Ar as a process gas, but many other gases can be used to similar effects including N₂, CF₄, and CH₄.

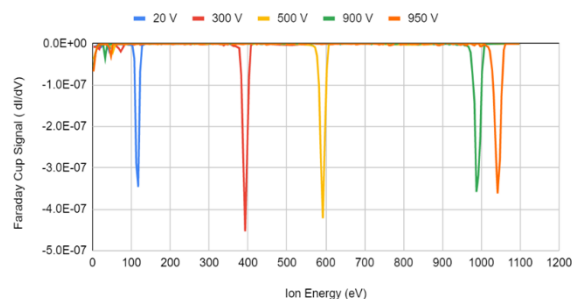


Figure 3. Faraday cup measurements of beam under various voltage conditions. A narrow range of ion energies is produced for excellent processing control.

While the design of the magnetic confinement enables good plasma uniformity along the full length of the source, we can tune the uniformity further by controlling the gas flow into the source. In order to demonstrate this, we setup a test in which we etched the surface of a thermal oxide coated silicon wafer, measuring the resulting optical thickness of the SiO₂ layer. The Figure 4 shows the results of this with a uniformity of better than 5% over 165mm of the 200mm source. We continue to improve this uniformity as we scale the source to larger sizes.

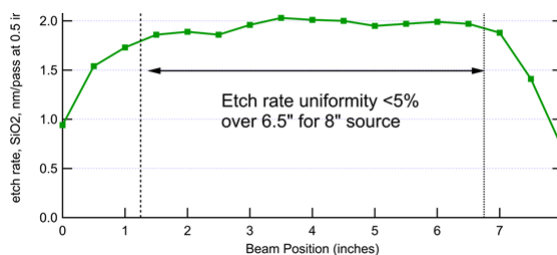


Figure 4. Film thickness uniformity data after etching a thermal oxide coated Si wafer.

With such a wide energy output range available, we are exploring many application areas including: ion assisted deposition (100 to 300 eV) for enhancement of thin silver, diamond-like carbon, and transparent conductive oxides; ion etching (0.3 to 10 keV) for patterning, ion beam sputter deposition and surface morphology modification; and ion implantation (up to 60keV) for anti-reflection treatments and surface nitriding. In this talk we will go into detail around the application and process results relating to ion implantation into glass and sapphire substrates for creating anti-reflection surfaces.

Traditionally, anti-reflection surfaces are created by the deposition of precisely structured multi-layer optical coatings using physical vapor deposition (sputtering, evaporation). These coatings have been refined and optimized over decades of work, enabling complex optical stacks. However, for many low margin products, these optical coatings are not economical to produce at scale and also do not survive well in demanding outdoor environments. Our approach is to physically alter the surface of the glass and change its refractive index at a controlled depth. This

is not a coating that can spall and scratch and fail. It is a modification of the substrate surface and it is as durable as the substrate itself. We achieve this by ion implantation.

The basic principle is to accelerate argon and/or nitrogen ions into the substrate surface. The ion energy, imparted by the source's accelerating voltage, along with additional process parameters, determines the depth of ion penetration into the surface. The ion dose, that is, the number of ions implanted is determined by the ion beam current and the treatment time. These two variables, ion energy and dose, allow control over the depth and refractive index of the optical layer. The refractive index of the layer is changed by the formation of a micro-porous region, lowering the density and lowering the refractive index.

The use of ion implantation for creating anti-reflection surfaces is a known and published technique.³ However, the use of implantation in high volume manufacturing has always been limited by the lack of a source capable of producing high ion currents over a large area. Our source technology has solved this underlying economic limitation.

Results

Several experiments were performed that demonstrate the tunability of the ion implantation process. In this report we show the effect of implant species type, ion energy, implant dose, and substrate type on the resulting surface reflectance of the samples under test. Specular reflectance of sample surfaces was measured by a Filmetrics F20 reflectometer. All data reported are for single surface reflectance with the backside reflection suppressed.

Our 200 mm ion source was installed within a horizontal in-line type plasma processing system built by the Malachite team. For all reported data, the ion source was configured with the beam angle perpendicular to the substrate surface. The system was evacuated to a base pressure of 5.0×10^{-7} torr prior to testing. The substrates were placed onto a graphite carrier and allowed to translate past the ion source at a controlled transport speed. The ion source control is such that the beam energy is set while the anode current is adjusted to produce the desired beam current. Implant dose is calculated from the beam current, the transport speed and the number of times the substrate passes the source.

The first experiment was a dose ladder in which Ar ions were accelerated to 50keV into 6mm thick soda lime glass (SLG). The data in Figure 5 demonstrate the ability to tune the position of the reflectance minima, while shifting the spectra $<0.5\%$. For visual comparison, a textured low-Fe solar glass was treated in a similar manner. An image of the resulting surface demonstrates the reflectance improvement (Figure 6).

Next, a dose ladder was completed with N_2 as the implant species at 40keV (Figure 7). A similar result was achieved as the Ar dose ladder in that the reflectance properties of the surface can be tuned and the minima can be positioned as desired for the end use application.

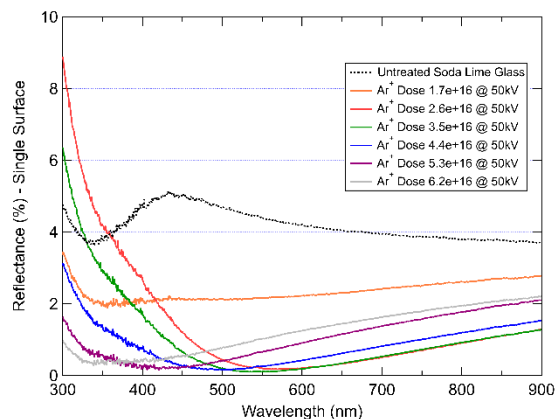


Figure 5. Argon dose ladder at 50kV ion energy into SLG



Figure 6. Image comparing visual reflectance change of treated vs untreated low-Fe glass used for solar applications.

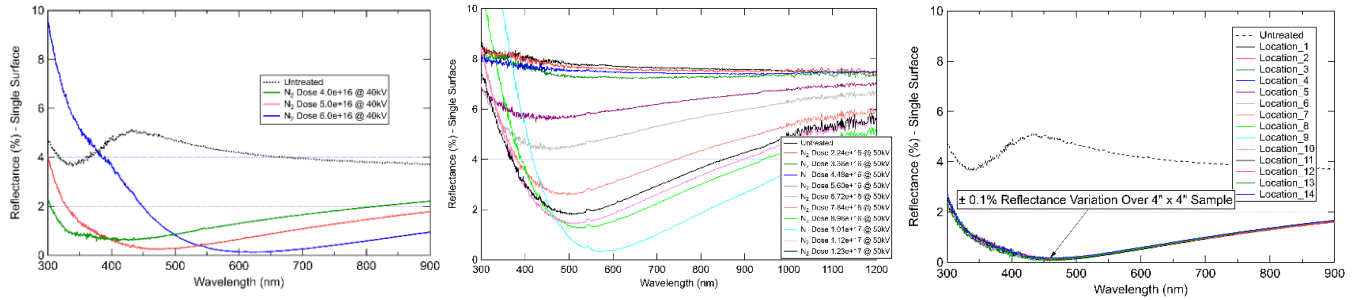


Figure 7. Nitrogen dose ladder at 40kV into SLG (left). N_2 dose ladder at 50kV into sapphire (middle). Uniformity of treatment over 100mm x 100mm SLG (right).

Several other substrate types were evaluated and demonstrated as viable candidates for the anti-reflection treatment. This includes, but is not limited to, SLG, low-Fe solar glass, chemically strengthened glass, tempered/non-tempered glass, and sapphire. Sapphire in particular was demonstrated to reduce the single side reflectance from 8% to $<0.5\%$ (Figure 7).

Working to optimize the processing for Ar implant into SLG we found we were able to achieve reflectance uniformity of better than $\pm 0.1\%$ and achieved a total reflectance reduction of $>80\%$ between 300nm to 900nm versus the untreated sample (Figure 7). In an optimized, high current source operation we have been able to achieve throughput of 1.5 m/min transport speed with a single source, single pass process.

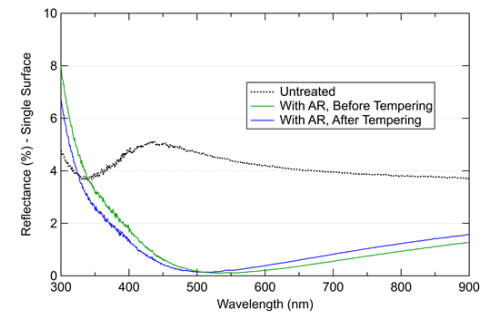


Figure 8. Reflectance measurement of sample before and after glass tempering process. Reflectance effect remains.

Finally, in order to demonstrate the durability of the treatment, implanted samples were subjected to glass tempering process (30min at 620°C) and the reduced reflectance surface remained (Figure 8). This is a promising result as it allows the treatment to be applied prior to the tempering processing commonly used in automotive applications.

Impact

Ion implantation into solids has become a critical tool of the semiconductor industry. However, despite a large body of literature demonstrating non-semiconductor applications, the technology has been confined to high value per area products. An extension of implant applications into commodity production of displays, photovoltaics, automotive components, and architectural glass has not been economically viable as implant technology has been incompatible with the multiple square meter per minute production rates.

The source technology that we have developed enables precisely controlled, high flux, high energy ion beams in a linearly scalable design. No other source technology is capable of this type of processing. We have demonstrated multiple ways in which to achieve an anti-reflection surface on multiple types of substrates with different implant conditions.

References

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Prior Publications: This is our first time submitting this source and application to the Display Week conference.