Optical properties of Ti and N implanted soda lime glass

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Soda lime glass was implanted sequentially with Ti^+ and N^+ to doses ranging from 2 to 30×10^{16} cm^{-2} in order to study the resulting optical properties. Analysis of the implant distributions was made by using Rutherford backscattering and x-ray photoelectron spectroscopy and revealed profiles which closely followed each other as designed by the selection of implant energies. Analysis of optical properties showed that the highest dose resulted in an increase in the fraction of infrared reflected by more than a factor of 4 versus 1.7 for the visible regime. The percentage of the total solar radiation rejected exceeded 60% at the highest dose, indicating that the buried layer is highly effective in reducing solar load. © *1995 American Institute of Physics.*

Implantation of selected ions into glass is known to affect optical properties in selected wavelength regimes. Reducing reflection of visible or transmission of UV or infrared (IR) radiation is of great practical importance in, for instance, solar load control. Achieving these properties through implantation has the advantages over coatings of no interface, potentially greater surface durability and use of less material. One such application is in the formation of a buried layer of TiN by sequential implantation of Ti and N. The formation of TiN by ion implantation was first demonstrated by Rai *et al.*,[1] who implanted 104 keV Ti^+ at 5×10^{17} cm^{-2} and 35 keV N^+ at 5×10^{17} cm^{-2}. Mazzoldi *et al.*[2] (190 keV Ti and 40, 70, or 100 keV N), Battagten[3] (190 keV, 5×10^{16} Ti^+ cm^{-2} and 70 keV, 2×10^{17} N^+ cm^{-2}), and Bertoncello[4] (30–190 keV, 5×10^{16} Ti cm^{-2} and 15–100 keV, $5–20\times10^{16}$ N cm^{-2}), all reported the formation of a titanium oxynitride (TiO_xN_y) following implantation into amorphous SiO_2. In this letter, we report on the implantation of Ti and N into soda lime glass and the resulting optical properties.

A total of five Ti and N implantations was made into 0.18 cm thick, clear float soda lime glass, a commercial product of the Glass Division of Ford Motor Company, of composition (weight percent) 73.3 SiO_2–13.6 Na_2O–8.6 CaO–4.0 MgO–0.2 Fe_2O_3–0.2 SiO_3–0.1 Al_2O_3. Implantations were performed in a sequential fashion with Ti implanted first. The TRIM (transport of radiation in matter) code[5] was used to determine the energies of Ti^+ and N^+ to produce overlapping concentration profiles. As such Ti^+ was first implanted at 87 keV to target doses of 2, 5, 8, 10, and 30×10^{16} cm^{-2}, followed by N^+ implantation at 30 keV to the same doses. Since the ion beam was N_2^+, the accelerating voltage was 60 kV. Implantations were made at a current density of $\sim$1 $\mu A/cm^2$ in a vacuum of $<1\times10^{-6}$ Torr. Implantations were nominally performed at room temperature, however, beam heating caused the surface temperature to rise by $\leqslant$200 °C. No postimplantation annealing was performed.

Analysis of the implants was performed by Rutherford backscattering spectrometry (RBS) using 2 MeV He^{++} at a scattering angle of 165°. RBS results indicate that the amount of retained Ti was 1.4, 3.2, 6.3, 7.4, and 23.0×10^{16} cm^{-2} with a peak Ti concentration of $\sim$40 at. % at the highest dose, and a mean depth of 19 nm following Ti implantation, Fig. 1. There was some loss (<10% of the amount present) of Ti following subsequent N implantation (probably due to sputtering). X-ray photoelectron spectroscopy (XPS) coupled with 5 keV Ar^+ sputter depth profiling was also conducted. Analysis was done with monochromatic Al $K\alpha$ (1486 eV) x-rays in a vacuum chamber at a pressure better than 1×10^{-9} Torr and was maintained at 1×10^{-7} Torr during argon sputtering. XPS was conducted on the sample receiving the highest dose and, as shown in Fig. 2, the Ti and N profiles track each other closely, peaking at concentrations of $\sim$30 at. %. These results are in close agreement with those of Mazzoldi *et al.*[2] who showed that at an energy ratio of 2.7; 190 keV (Ti) to 70 keV (N) (versus 2.9 for our experiments), the implanted N profile closely follows the Ti profile.

Optical property measurements were made with a Perkin–Elmer LAMBDA9 UV/VIS/NIR spectrophotometer. The instrument is a double-beam instrument and it was op-

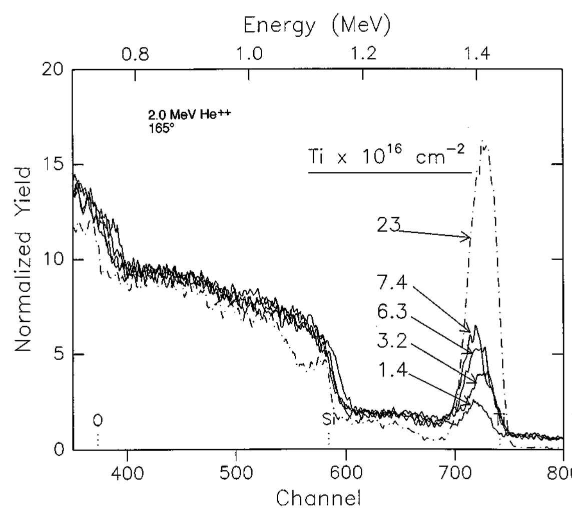

FIG. 1. Rutherford backscattering spectra of Ti implantations showing retained amounts prior to N implantation.

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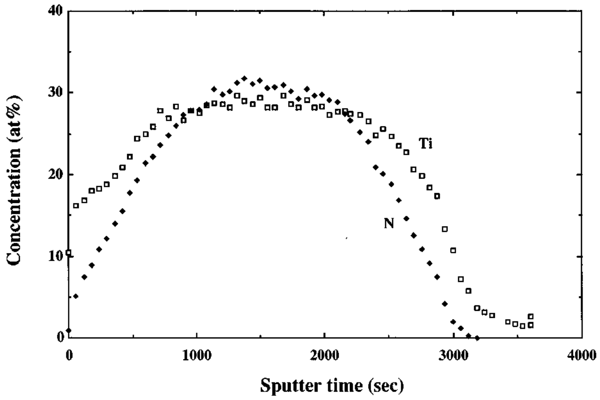

FIG. 2. Ti and N concentration profiles during sputter depth profiling as measured using XPS, for Ti and N doses of 3×10^{17} cm^{-2} (retained dose $\sim2.3\times10^{17}$ cm^{-2}).

erated in the "VW" configuration with an absolute specular reflectance accessory. The reflectance is measured at a fixed angle of 7.5°. Data are reported as percent reflected and percent transmitted as a function of wavelength for the various implantations. Wavelength ranges are as follows: ultraviolet; 280–400 nm, visible; 400–720 nm, infrared; 720–2120, and total solar radiation wavelength range; 280–2120 nm. Figure 3 shows the percent of radiation reflected for clear and Ti+N implanted glass for three wavelength regimes defined previously. The percent transmission and percent reflection as a function of wavelength for the highest dose (2.3×10^{17} cm^{-2}) are shown in Figs. 4(a) and 4(b), respectively. In all cases, the radiation is incident on the treated side of the glass. Note the sharp rise in the IR reflection at the highest dose of 2.3×10^{17} cm^{-2} Note also that the % rejected exceeds 60% at this dose. This is the percent of incident solar radiation that is rejected, i.e., not transmitted by the glass. It is a combination of the amount of energy reflected and the amount of energy absorbed and transmitted by conduction to the outside and therefore, is of great practical value. It also depends on the emittance of the glass and the flow of air across the outside surface and is calculated using the code, MULTFILM.[6] Also of practical significance is the comparatively small increase in

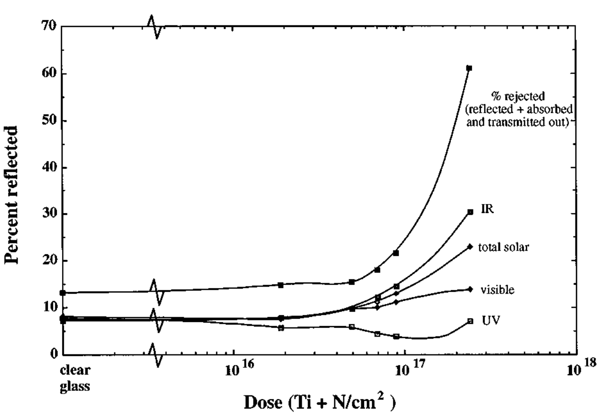

FIG. 3. Percent of incident radiation reflected vs dose for selected wavelength ranges.

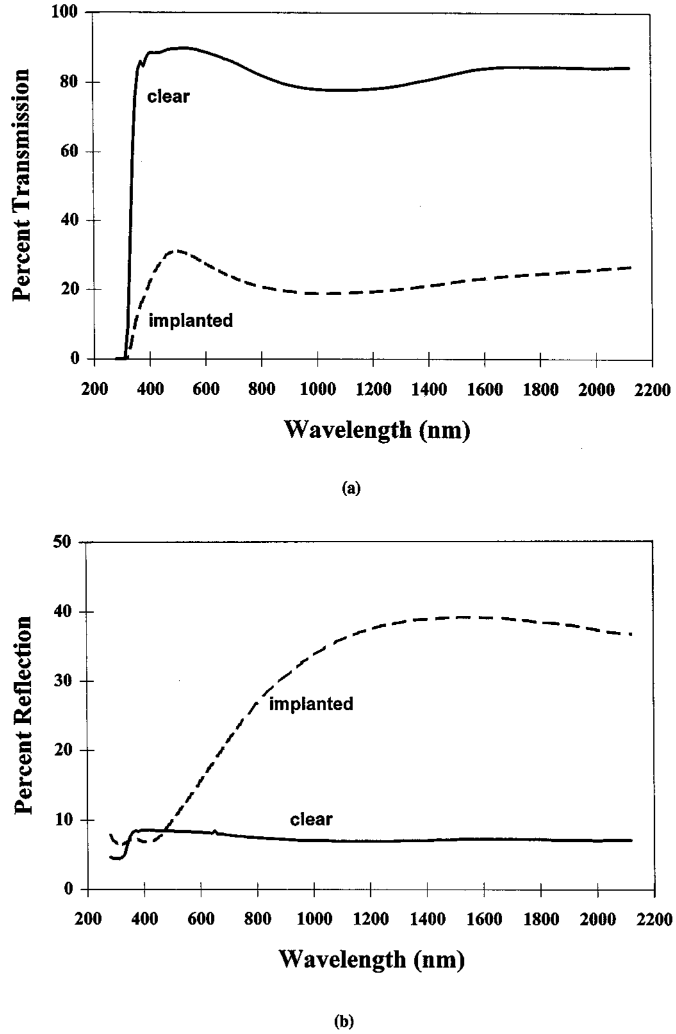

FIG. 4. Percent transmission (a) and percent reflection (b) vs wavelength for Ti+N implanted (2.3×10^{17} cm^{-2}) and clear glass.

visible light reflected over the entire dose range. Calculations were performed using MULTFILM for a pure, 50 nm thick TiN layer on soda lime glass and yielded a reflection of 32.8% in the IR range and a total rejection of 64%. On the basis of either the % IR reflected or the % rejected, it is evident that the implanted layer performs nearly as well as a pure TiN film of thickness 50 nm.

The abrupt increase in IR reflection and total solar load rejection at high dose were accompanied by a change in the color of the glass from a metallic silver to a distinct gold color. Although the existence of a TiN phase was not verified, the color change and optical performance strongly suggest its presence. While optimization of implantation parameters has not yet been completed, these preliminary results clearly indicate the potential for achieving substantial gains in solar load rejection through the formation of buried layers by ion implantation.

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