LOW ENERGY PROTON IMPLANTATION TECHNIQUES FOR COVERGLASS IRRADIATION QUALIFICATION

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ABSTRACT

It is demonstrated that the two hydrogen concentration profiles and the associated effects on solar cell coverglass degradation created at equivalent atomic fluences of 7.4×10^{15} particles/cm^2 using 30 keV proton (H^+) and 60 keV diatomic hydrogen ion (H_2^+) implantation on solar cell coverglass material are nearly identical. Both Monte Carlo simulation and experimental results support this contention to the level of acceptable experimental error, thereby enabling coverglass radiation testing to be performed using the latter, more cost effective option.

INTRODUCTION

Space particle radiation damage to solar cell coverglass has the detrimental effect of decreasing the optical transmission in low wavelength regions. This can affect the solar cell collection efficiency, especially in solar cells which rely on low wavelength absorption. Figure 1 shows some general information demonstrating this effect. In Fig. 1, the AM0 light emission spectrum (black) is plotted along with quantum efficiency (QE) measurements on a standard triple junction $InGaP_2$/GaAs/Ge solar cell as a function of wavelength to a maximum of 1200 nm. The QE for each subcells is plotted individually using the proper light and/or electrical biasing techniques. Also plotted are transmission data for both unirradiated (solid

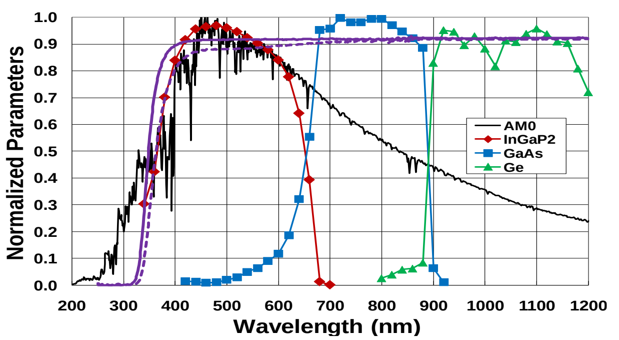

Figure 1. Impact of coverglass radiation damage on multijunction (3J) solar cells. The low wavelength regions are preferentially affected by irradiation.

purple) and irradiated (dashed purple) coverglass material. One can see from this data that the radiation damage in the coverglass can preferentially deprive the $InGaP_2$ top cell from collecting light in the low wavelength region. This effect is not as critical in practice for this solar cell design, as the cell quantum efficiency will also degrade as the radiation damage level is increased. In the 3J $InGaP_2$/GaAs/Ge design, it has been shown that the middle GaAs subcell eventually becomes the current collection limiter. Therefore, light starving the top $InGaP_2$ subcell may not be that important for current collection in the overall 3J device. However, the coverglass degradation will affect the open circuit voltage of the $InGaP_2$ cell since all subcell voltages add in the 3J stack. While these effects are small, the impact on cell efficiency justifies a reasonable level of care in the solar cell design and the coverglass properties to avoid significant impacts from coverglass degradation.

A common specification in solar cell coverglass radiation testing is to use 30 keV protons (H^+) irradiated to a fluence of 7.4×10^{15} H^+/cm^2. This ground-based test does have some practical significance as can be seen in Fig. 2, where the particle radiation spectra for a typical 15 year mission for a geosynchronous (GEO) orbit are shown. The radiation spectra in Fig. 2 were obtained using SPENVIS [1] where the AP8 and AE8 proton and electron

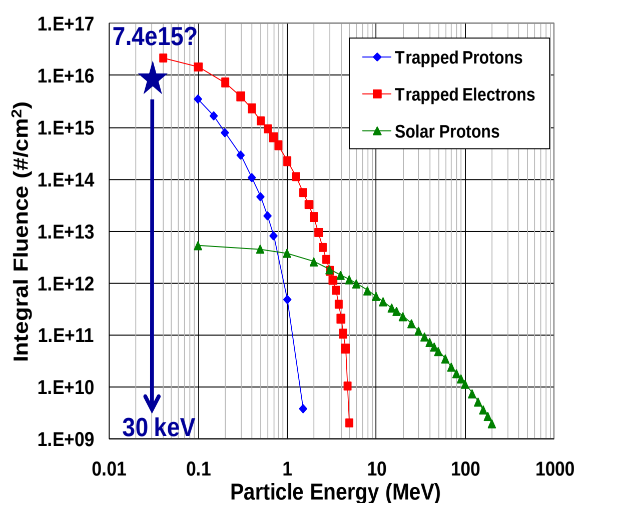

Figure 2. Particle radiation environment for a 15 year geosynchronous (GEO) orbit.

environment models, as well as the ESP Total Fluence solar proton model (95% confidence) were employed. The 30 keV proton specification of 7.4×10^{15} H^+/cm^2 can be seen to exist from a low energy extrapolation of the trapped proton data. This low energy proton implantation is also chosen to deposit a large ionizing dose in a shallow

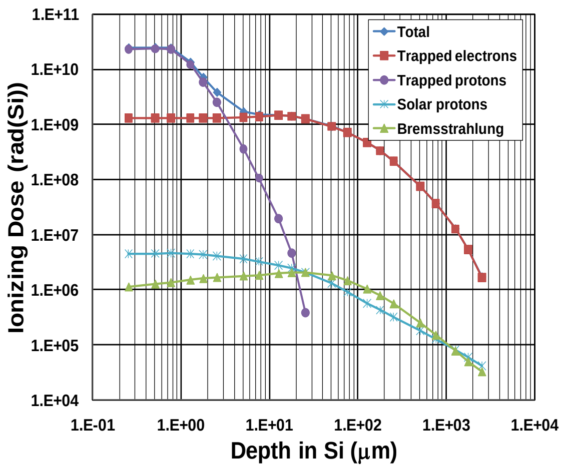

Figure 3. Ionizing dose-depth curve for the radiation environment of the 15 year geosynchronous (GEO) orbit show in Fig. 1. The trapped protons are the most damaging to shallow surfaces in a GEO-based design.

region (like a coating) since 30 keV protons have a range of about 0.33 μm in glass. Low energy proton ground testing is also important considering the ionizing radiation dose-depth profile for this 15 year GEO orbit.

The problem with this irradiation specification is that most implantation facilities cannot produce 30 keV protons with high beam fluxes, thereby requiring long exposure times and, hence, increased cost. In similar circumstances commercial ion implantation facilities overcome this issue by using the more accessible and abundant diatomic hydrogen ion (H_2^+) at double the energy and half the particle fluence (see Fig. 4). For example, to get a fluence of $7.4x10^{15}$ of 30 keV H^+/cm^2, one needs only a fluence of $3.7x10^{15}$ using 60 keV H_2^+/cm^2 to get the same effect. Most commercial ion implantation facilities can get much more than twice the beam current using 60 keV H_2^+ ions over 30 keV H^+ (a consequence of the ion source technologies employed) thereby saving time and cost in radiation testing and other applications without losing test/or process fidelity. This paper will show results, both theoretical and experimental, ~~to~~ demonstrating the equivalence of this approach as a material testing methodology.

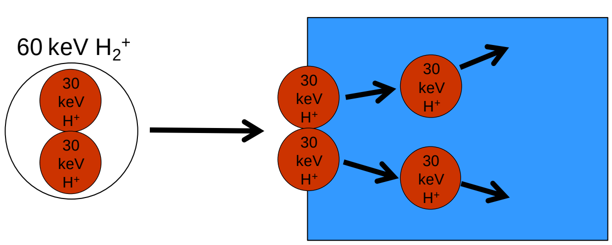

Figure 4. Schematic of the dissociation of a 60 keV diatomic hydrogen ion (H_2^+) into two 30 keV protons (H^+) upon impingement upon a material.

PROTON VS DIATOMIC HYDROGEN ION IMPLANTATION

The idea of using diatomic hydrogen ions to simulate the effects of protons has been documented before [2-7]. Because the binding energy of diatomic molecules is so low (~few eV) the molecules are readily dissociated upon impact with a material over very small distances (few atomic layers). Figure 4 gives a schematic of the assumed process. When a molecular ion enters a solid, its binding electrons are stripped away in the first few atomic layers and the resulting nuclear cluster immediately begins to expand due to the Coulomb repulsion between the separate atoms. As the "molecule" expands, the separation can become large enough after which the cluster will act as two independent particles. This process is commonly called a "Coulomb explosion". For diatomic hydrogen ions, the resulting irradiation by H_2^+ ions having energy *2E* acts to implant 2 protons (H^+) at energy *E*.

This process has been used to good effect in the qualification of secondary ion mass spectrometry (SIMS) systems [3] and is most commonly used in many semiconductor applications such as: 1) the creation of a high concentration of hydrogen layers in silicon as part of the "smart cut" process involved in silicon on insulator (SOI) technologies [7] and 2) converting regions of semi-insulating compound semiconductor materials into insulating (therefore isolating) regions between devices such as HBTs or VCSELs (commonly referred to as transmutation doping). In applications requiring the extension of ion implantation tooling into low energy doping applications, the semiconductor industry has also resorted to equivalent multiatomic substitutions for processes normally thought of in terms of monatomic ions. At effective atomic energies between 0.25 keV and 20 keV it sometimes becomes more productive to substitute As_4^+ or As_2^+ for As^+. Also, equivalent substitutions are sometimes made for phosphorus ion states and there is a large body of work on the substitution of monatomic boron ions with decaborane and octadecaborane.

We will now show Monte Carlo simulation and experimental evidence to support the substitution of diatomic hydrogen ion for protons using coverglass material.

SRIM Monte Carlo Transport Simulation

To simulate the transport of protons and ions into materials, the Monte Carlo transport program SRIM [8] was employed. The simulation structure was comprised of a 100 nm MgF_2 (ρ=3.18 g/cm^3) antireflection coating on top of borosilicate glass (ρ=2.584 g/cm^3). The 30 keV proton transport simulation is performed in a routine fashion using SRIM. However, to simulate the effect of diatomic hydrogen ions in SRIM, it was necessary to manipulate the program inputs to identify the correct charge state while also having the correct mass, so the

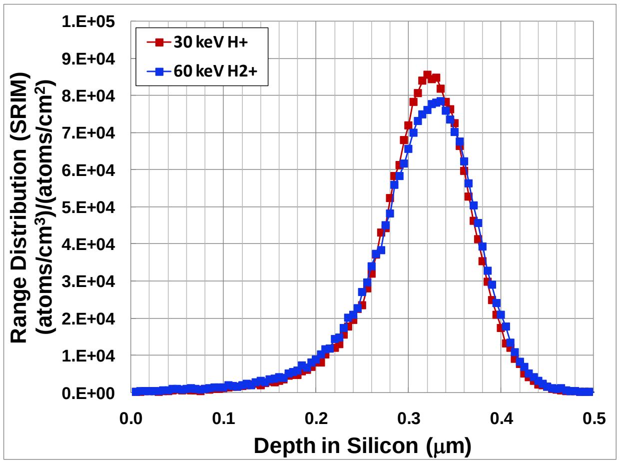

Figure 5. SRIM simulation of 30 keV H^+ and 60 keV H_2^+ into borosilicate glass coated by 100 nm of MgF_2.

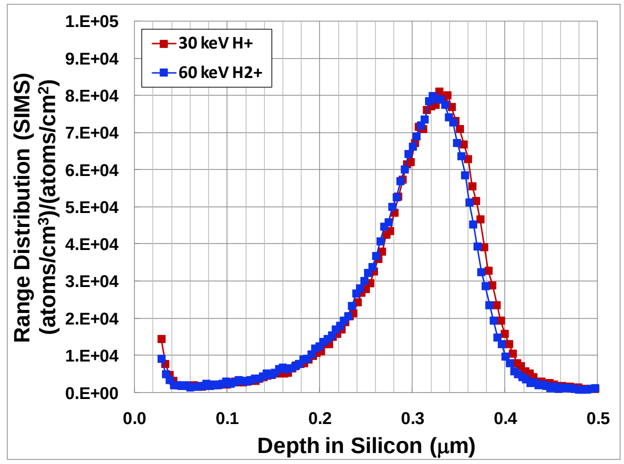

Figure 6. SIMS results on silicon samples that have been implanted by both 30 keV H^+ and 60 keV H_2^+.

Table I. SRIM simulation range data of 30 keV H^+ and 60 keV H_2^+ into 100 nm of MgF_2 and borosilicate glass.

Implanted Particle	Peak Range (µm)	Peak Concentration (cm^{-3})
30 keV H^+	0.320	8.552×10^4
60 keV H_2^+	0.335	7.854×10^4

Table II. SIMS range statistics of 30 keV H^+ and 60 keV H_2^+ into silicon wafer material.

Implanted Particle	Peak Range (µm)	Peak Concentration (cm^{-3})
30 keV H^+	0.334	7.957×10^4
60 keV H_2^+	0.327	7.914×10^4

simulation was done using helium atoms simulated at one-half the mass [9]. The results of these Monte Carlo simulations are shown in Fig. 5 where the hydrogen atom distributions are plotted as a function of distance in the structure, normalized to unit incident particle fluence. Both the 30 keV proton and 60 keV diatomic hydrogen implantation simulations are seen to agree quite well. Table I gives the details regarding the peaks for these SRIM simulations. The difference in depth relating the peak concentrations is determined to be only ~15 nm. The peak concentrations also differ, with the 30 keV proton implantation yielding ~10% higher concentration. These Monte Carlo simulations have been useful in qualitatively modelling monatomic and diatomic hydrogen implantation. However, more substantial data was needed to confirm the premise of equivalence for this purpose of H^+ vs H_2^+ implantations.

Secondary Ion Mass Spectrometry (SIMS) Analysis

Secondary ion mass spectrometry (SIMS) [10] is a technique used in materials science and surface science to analyze the composition of solid surfaces and thin films by sputtering the surface of the specimen with a focused primary ion beam and collecting and analyzing ejected secondary ions. These secondary ions are measured with a mass spectrometer to determine the elemental, isotopic, or molecular composition of the surface. SIMS is the most sensitive surface analysis technique, being able to detect elements present in the parts per billion range. This technique was used to determine the hydrogen implantation profiles in irradiated silicon.

To confirm the method proposed by Innovion Corporation we performed control 30 keV proton irradiations at a fluence of 5×10^{14} H^+/cm^2 and experimental 60 keV diatomic hydrogen ions at a fluence of 2.5×10^{14} H_2^+/cm^2 on silicon wafer material. The samples were shipped to Evans Analytical Group [11] for SIMS measurements to obtain hydrogen implantation profiles as a function of depth. Figure 6 shows the results of those measurements with Table II giving numerical information. This comparison is excellent, with the peak depth differing by just slightly over 2% (7 nm out of 330nm) and the peak concentration differing by less than 1%. This seems to be quite compelling evidence that our premise was indeed valid.

The damage distribution is expected to follow the physics presumed by the SRIM modelling program, however, there are mechanisms that can alter or redistribute the hydrogen concentration profile. The agreement between the two profiles argues that it is unlikely that a redistribution of either profile has occurred. Furthermore, the absence of noticeable deviations from the ideal profile shape predicted by the SRIM program also supports the profiles being "as implanted" . This in turn would imply the damage profiles would be expected to be equivalent and therefore the impact on coverglass degradation would be expected to be equivalent. To propose equivalence for the testing of coverglass it remained necessary to eliminate the prospect of a difference between atomic concentration distributions and the effective degeneration of the coverglass. To show this, transmission measurements on irradiated glass material are needed.

Optical Transmission Measurements on QIOPTIQ CMG Coverglass

To relate the degradation of the coverglass to the hydrogen concentration profiles, particle irradiations on coverglass material were performed at Innovion Corporation using an Eaton 6200 class serial end-station ion implanter using 30 keV H^+ and 60 keV H_2^+ at particle fluences of $7.4x10^{15}$ and $3.7x10^{15}$ particles/cm^2, respectively. The sample temperatures were kept below 40°C during the irradiations. Sample uniformity was controlled by a raster process. Dosimetry was controlled by a current integrator. The configuration of this tool's end-station essentially comprises a of target chamber which allows 150 mm wafers of silicon or other materials to be serially positioned at the deepest end of the electro-statically suppressed Faraday structure. Before and after the irradiations, transmission measurements were performed at Qioptiq Space Technology using a Perkin Elmer Lambda 9 spectrophotometer. Two types of Qioptiq CMG coverglass types were considered in this experiment: 1) CMG 75 CC/AR (conductive/anti-reflection coated) and 2) CMG 100 AR (anti-reflection coated). The thicknesses of the coatings are on the order of 100 nm.

Figure 7 shows the percent transmission results for the CMG 75 CC/AR coverglass under the irradiations described above. The radiation effects are seen to affect the blue part of the wavelength spectrum, consistent with measurements from facilities used previously. It is shown in Fig. 7 that the differences between the two ion species (H^+ and H_2^+) are barely visible. Figure 8 shows the same data from Fig. 7 plotted as a percent difference from the unirradiated condition, which allows us to more clearly see the differences between the effects of the different radiations. The worst degradation occurs at about 350 nm

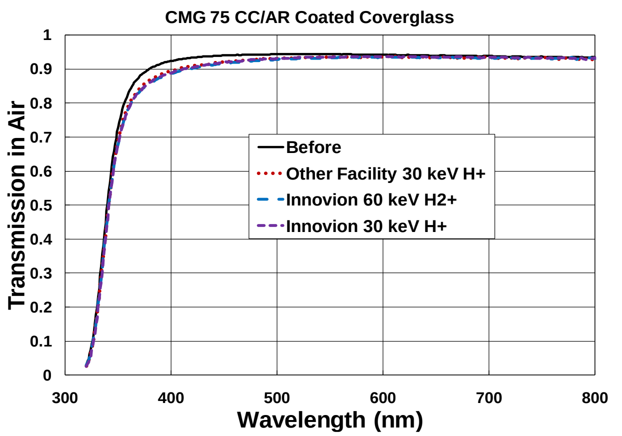

Figure 7. Transmission measurements on Qioptiq CMG 75 CC/AR coverglass before and after exposure to both 30 keV H^+ and 60 keV H_2^+ ions. The fluences were $7.4x10^{15}$ and $3.7x10^{15}$ particles/cm^2, respectively.

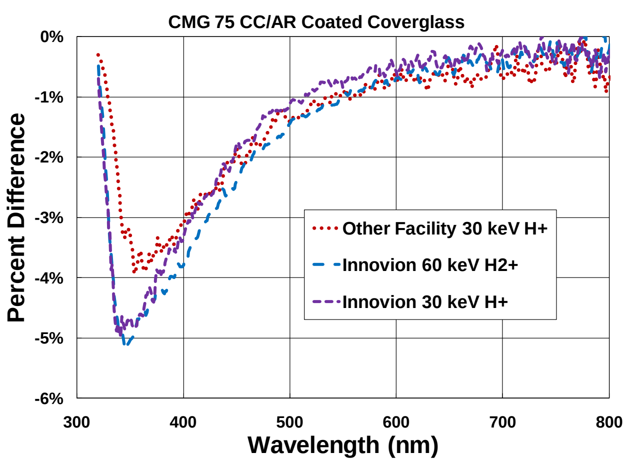

Figure 8. Percent degradation of the data given on Fig. 7 above.

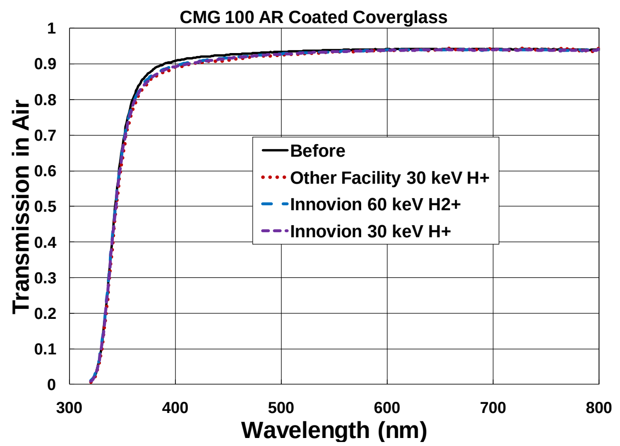

Figure 9. Transmission measurements on Qioptiq CMG 100 AR coverglass before and after exposure to both 30 keV H^+ and 60 keV H_2^+ ions. The fluences were $7.4x10^{15}$ and $3.7x10^{15}$ particles/cm^2, respectively.

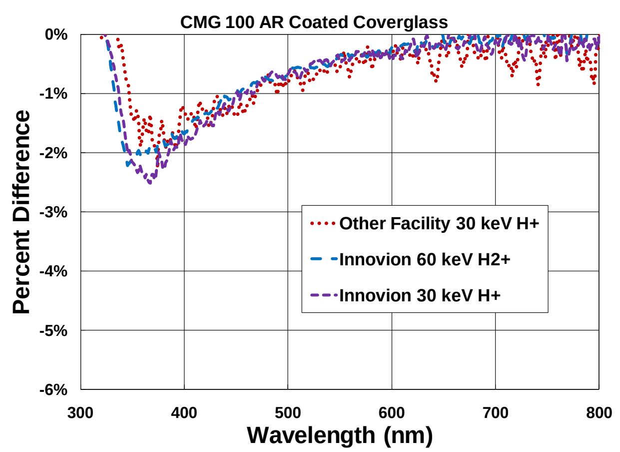

Figure 10. Percent degradation of the data given on Fig. 9 above.

and is about a 5% effect for this coverglass type. The differences between the 30 keV H^+ and the 60 keV H_2^+ implantations are very small and are assumed to be within the experimental uncertainty of the measurement system. Figures 9 and 10 show results in the same manner as for Figs. 7 and 8 for the case of CMG 100 AR coverglass. Again, the differences are quite small between the two irradiating species and are again assumed to be within the experimental uncertainty of the measurement system.

DISCUSSION

A simulation using the widely accepted SRIM program and three data sets are presented here which all show that the effects of 30 keV proton (H^+) and 60 keV diatomic hydrogen ions (H_2^+) are very similar in nature. For the conditions often used for coverglass radiation testing, the peak locations lie at an approximate depth of 330 nm. The SRIM simulations (Fig. 5) did show some differences in both the peak position (15 nm) and peak concentration (~10%) but neither was confirmed by the data sets. Recall that these simulations were performed on a 100 nm MgF_2-coated borosilicate glass. Although the differences in the SRIM simulations may seem to be small for this case, it may be more important for~~when~~ different materials having different thicknesses, etc. For most coverglass materials, the applied coatings are thin enough that the peak damage concentrations for such irradiations are well beyond interfaces and lie exclusively within the glass itself. Nevertheless, these simulations did give us a simple "first step" in this experimental comparison.

The SIMS measurements showed a much more compelling result than did the SRIM simulations. Indeed, the results (Fig. 6) showed a much better agreement between ion species than predicted by simulation, with the peak positions (~7 nm) and peak concentrations (<1%) being in closer agreement. However, two things need to be stated regarding the SIMS experiments. Firstly, the SIMS measurements were performed on bare silicon wafer material and not actual coated coverglass material. Secondly, the implantation fluences were 2.5-5x10^{14} particles/cm^2 and not representative of the required specification as described above (7.4x10^{15} H^+/cm^2).

Magee and Wu [3] analyzed implants of H^+ and H_2^+ into silicon as part of an evaluation of the sensitivity and depth resolution of the SIMS technique for hydrogen depth profiling. Comparing the hydrogen profiles in silicon using 80 keV H^+ and 160 keV H_2^+ at fluences of 1.2x10^{16} and 0.6x10^{16} particles/cm^2, respectively, there was a noticeable peak shift in depth in the SIMS results. The diatomic hydrogen implant produced a peak shifted approximately 40 nm (~6% from the proton peak at ~0.65 μm) to a shallower position as that compared with the proton implant. Other implants were undertaken to study this effect using lower fluences (1.0x10^{15} H^+/cm^2 and 0.5x10^{15} H_2^+/cm^2) and energies (30, 40, 50, 60, 80, 100, 120 and 140 keV protons) resulting in no distinguishable shift in the peak position. The decreased range of the diatomic hydrogen ion implant as compared to the proton implant was attributed to an increase in sample damage associated with the molecular implant due to the dissociation process. The threshold fluence level for this process for proton energies >30 keV was therefore determined to be >10^{15} H^+/cm^2. It is unclear from the Magee and Wu work [3] what the implant peak shift would be comparing 30 keV H^+ and 60 keV H_2^+ when irradiated to 7.4x10^{15} and 3.7x10^{15} particles/cm^2, respectively. However, if the effect were related to ionizing stopping power data for protons in silicon, it is estimated that the effect will be lessened using the lower energies. The stopping powers for 80 and 30 keV protons in silicon are 533 and 501 MeVcm^2/g, respectively. This means that 80 keV protons in silicon cause ~6% more ionization damage than do 30 keV protons. It should be noted that, if displacement damage is determined to be the root cause of the peak shift, the NIEL ratio comparing the two protons in silicon predicts roughly twice the displacement damage from 30 keV over 80 keV protons. Taking onto account the nonuniformity of the implantations using these energies, the damage ratio would even be higher [12].

There has been significant work on hydrogen implantation on silicon wafer thereby establishing the redistribution of the hydrogen concentration profile as a function of temperature experienced during the implantation process. It seems plausible that the different implant conditions used to prepare the samples might have allowed sufficient heating to promote differences in the redistribution process. This in turn likely affected the validity of this comparison and at conditions maintaining lower temperatures the difference might not have occurred. The higher energies and higher doses and especially the higher beam currents available for the diatomic hydrogen sample preparation would be expected to redistribute the hydrogen in that sample toward the surface as observed. In this work the sample temperature during implantation was kept low enough (<40^{o}C) to likely eliminate or minimize the effect of such a redistribution mechanism.

Clearly, more measurements would elucidate these effects. Specifically, SIMS measurements as a function of energy and fluence on actual coverglass materials would be beneficial. However, for the usual thin coatings on coverglass material, the peak shifts are still considered to be inconsequential. Furthermore, it is not clear that one can detect such small differences with optical transmission measurements.

CONCLUSIONS

In the radiation qualification of coverglass material for use in the space radiation environment, it has been shown that the effect of 30 keV protons can be obtained using 60 keV diatomic hydrogen ions at one-half the particle fluence. For the thin film coatings tested, the equivalence of these methodology has been demonstrated using Monte Carlo simulations, SIMS measurements and optical transmission measurements. The equivalence of these methodologies with respect to range and damage in thick multi-layer films, of varying materials and densities, still needs to be ascertained.

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