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Tritiation of amorphous and crystalline silicon using T_2 gas

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Incorporation of tritium in hydrogenated amorphous silicon (a-Si:H) and crystalline silicon (c-Si) at 250 °C using tritium (T_2) gas at pressures of up to 120 atm is reported. The tritium is stored in a surface layer which is approximately 150 and 10 nm for a-Si:H and c-Si, respectively. The concentration of tritium occluded in planar and textured c-Si is linearly dependent on the total surface area. The tritium is stable and the dominant tritium evolution occurs at temperatures above 300 °C. The concentration of tritium locked in a-Si:H and c-Si was 20 and 4 at. %, respectively. Self-catalysis appears to be important in the tritiation process. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2234844]

With the continual miniaturization of microelectronics and its corresponding reduction in power requirements, there is growing research interest in the development of on-chip radioisotope micropower sources.[1,2]

Tritium, a radioisotope of hydrogen, is arguably the ideal candidate for such nuclear battery applications. Tritium has a half-life of 12.3 years. It decays to $^3He^+$ and releases energetic electrons with an average energy of 5.7 keV and a maximum energy of 18.6 keV. Considering that the threshold electron energy for disruption of the silicon lattice due to knock-on collisions is 20 keV, tritium decay beta particles pose little radiation damage concern for on-chip energy conversion devices. Safe tritium handling has been well studied and considerable experience has been gained from its wide usage in radioluminescent structures, pharmaceutical drug development, and fusion fuel research.[3] Finally, tritium is readily and economically accessible.[1,2]

Unfortunately, tritium in the gaseous form at standard conditions has a low power density of 87 $\mu W/cm^3$. Moreover, stable incorporation of tritium into semiconductor materials at sufficiently high power density is challenging. Possible approaches to high-density tritium incorporation include metal tritide films, formed by tritiation of evaporated hydride forming metals,[3] and tritiated amorphous silicon films, deposited using a plasma enhanced chemical vapor deposition (PECVD) technique.[1] Both methods, while practical, are relatively complicated.

In this letter we demonstrate a simple and versatile method to incorporate high-density tritium into various forms of silicon by exposing these to tritium gas. Stable and high-density tritium bonding in hydrogenated amorphous silicon (a-Si:H) and crystalline silicon (c-Si) structures was achieved. Posthydrogenation has been widely researched for passivation of amorphous silicon (a-Si) and a-Si:H. Hydrogen is incorporated into a-Si and a-Si:H by ion implantation or exposing the samples to monatomic hydrogen, hydrogen plasma, and H_2 gas at high temperatures.[4] Postdeuteration has also been investigated, and it has been shown that there is no chemical difference between hydrogen and deuterium.[4] Hydrogen has also been introduced into c-Si using similar processes. Considering that tritium is chemically identical to hydrogen and deuterium, it is proposed that similar processes can also be used to incorporate tritium into amorphous and crystalline silicon, thereby facilitating the integration of a radioisotope micropower source on chip. It is commonly accepted that hydrogen diffusion in silicon is predominantly in the atomic form and that posthydrogenation using molecular hydrogen gas typically begins with the dissociation of hydrogen molecules at the silicon surface. In void rich material, diffusion of molecular hydrogen is possible.[5] It is expected that tritium dispersion will also proceed in a similar manner. However, given the radioactive properties of tritium it is expected that tritium incorporation may be self-catalyzed, specifically, excitation, ionization, and dissociation of molecular tritium (T_2) by the energetic beta particles as well as the production of atomic tritium due to tritium decay.

In order to attain a high concentration of tritium in various forms of silicon, samples of silicon were exposed to tritium gas at a range of pressures at relatively low temperatures. The tritium loading system is described elsewhere.[6] Tritium pressures of up to 120 atm at 250 °C can be attained. All a-Si:H samples used in these experiments were prepared on crystalline silicon substrates, at various temperatures, using the dc saddle-field PECVD technique.[1]

To determine the tritium concentration and its bonding characteristics, thermal effusion experiments were carried out on tritiated samples at a linear ramp rate of 10 °C/min.[7] A typical temperature profile of tritium effusion from a 300 nm thick tritiated a-Si:H film is shown in Fig. 1(a). The sample, which contained 20 at. % hydrogen, was exposed to tritium gas for 9 days at a pressure of 120 atm and a temperature of 250 °C. The effusion profile shows that tritium is stably incorporated in a-Si:H film with essentially no effusion below 200 °C. Significant tritium effusion commences

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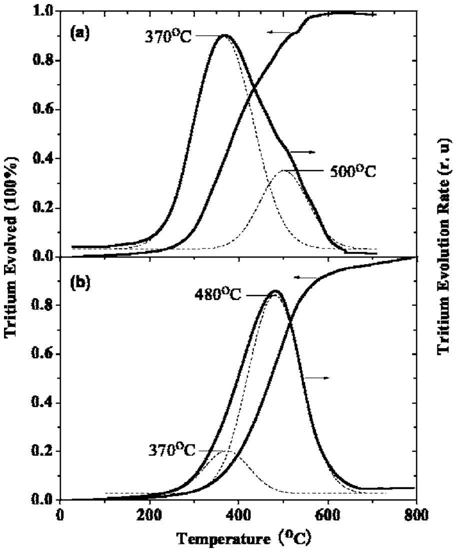

FIG. 1. Cumulative tritium effusion and tritium effusion rate as a function of temperature for silicon samples exposed to tritium gas at 120 atm and 250 °C: (a) *a*-Si:H and (b) *c*-Si. The dashed lines show the effusion peaks obtained by Gaussian deconvolution; the corresponding peak temperatures are indicated.

at the loading temperature of 250 °C and by 600 °C essentially all the tritium is evolved from the sample. A concentration of 7 $\mathrm{mCi/cm^2}$ was measured by thermal effusion from a 2 $\mathrm{mm^2}$ sample,[7] which is equivalent to an estimated average tritium atomic concentration of 10% after discounting for the tritium in the substrate. Using secondary ion mass spectroscopy (SIMS) we have determined that the tritium penetration depth in amorphous silicon is 150 nm, hence a more representative average atomic tritium concentration in *a*-Si:H is 20 at. %. The majority of the tritium evolution occurs around 400 °C. Gaussian deconvolution of the effusion rate reveals two effusion peaks, a dominant peak at 370 °C and a smaller peak at 500 °C. The low temperature peak is attributed to weak bonds, such as higher order tritides and clusters, and the high temperature peak to predominantly monotritide bonds.[7] The nature of tritium bonding is further examined through a Fourier transform infrared (FTIR) study. The infrared absorption spectra of the *a*-Si:H sample before and after the tritium exposure are shown in Fig. 2. The vibrational spectra show a peak at 2000 $\mathrm{cm^{-1}}$ which corresponds to the Si–H stretching mode. The additional peak in the spectrum for the tritiated sample at ~1200 $\mathrm{cm^{-1}}$ corresponds to the Si–T stretching mode. This FTIR result is consistent with the reported vibrational spectra of *a*-Si:H:T prepared by PECVD.[8]

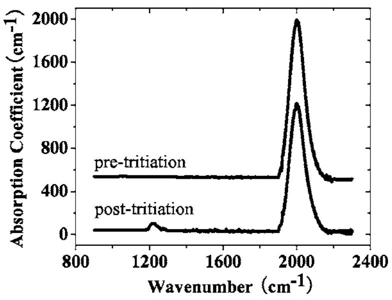

FIG. 2. IR absorption spectra of a *a*-Si:H film before and after tritium exposure. For clarity, the spectrum of the *a*-Si:H before tritium exposure has been shifted up by 500 $\mathrm{cm^{-1}}$.

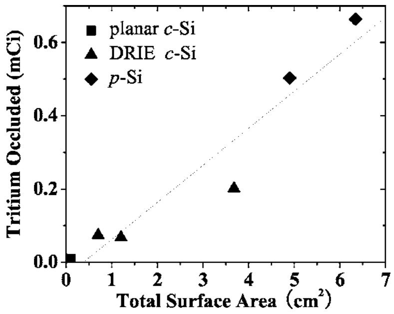

FIG. 3. Total tritium occluded in crystalline silicon as a function of the total surface area. Total surface area represents the actual surface area of the sample. The line is drawn as a guide to the eye.

Effusion measurement of a 500 μm thick planar *c*-Si sample, exposed to tritium for 3 days under similar conditions to those for the *a*-Si:H sample, reveals a relatively much lower tritium incorporation concentration of 0.1 $\mathrm{mCi/cm^2}$. Using the tritium penetration depth of ~10 nm, as determined from SIMS measurements, the average atomic concentration of tritium in *c*-Si is 4%. The average tritium concentration is five times lower than that in the *a*-Si:H film, a reflection of the much tighter lattice configuration of *c*-Si in relation to the defect prone network of *a*-Si:H. The effusion data for the tritiated *c*-Si sample are shown in Fig. 1(b). Gaussian deconvolution of the effusion rate profile shows two effusion peaks at 370 and 480 °C. In this case, the larger effusion peak at the higher temperature indicates that tritium is predominantly bonded in the monotritide form. FTIR measurement of the *c*-Si sample did not yield a tritium signal due to the low tritium content.

The influence of helium accumulation with tritium decay has not been investigated. It is expected that the effect of helium accumulation in amorphous and crystalline silicon will be quite different considering the inherent defect prone network of *a*-Si:H in contrast to the regular lattice of *c*-Si. One might expect the extent of lattice disruption and rearrangement to be small in *a*-Si:H in comparison with that in *c*-Si. In fact, the tritiated amorphous silicon samples prepared using PECVD techniques show no evidence of blistering after more than 6 years of aging.[1]

Tritiation of *c*-Si was further studied on trenched *c*-Si and porous crystalline Si (*p*-Si). Trenched *c*-Si samples were prepared by a deep reactive ion etching (DRIE) process, while *p*-Si samples were prepared using an electrochemical etching technique. The DRIE process produced an array of pores with diameter of 10 μm and depth of 120 μm. The surface area was effectively increased by 9, 30, and 33 times using different pore densities, in relation to the planar *c*-Si sample. The pore diameter of the *p*-Si was 2 μm and the depth was 150 μm. In this case the surface area was increased by 120 and 180 times for *p*-Si samples having pore distributions that were random and ordered pores, respectively. All DRIE *c*-Si and *p*-Si samples were tritiated under the same conditions as those for planar *c*-Si. Effusion experiments were carried out immediately after tritium loading. Figure 3 shows the total tritium evolved from these samples as a function of the corresponding total surface area, which includes the internal area of the pores. In spite of the different fabrication methods, Fig. 3 reveals a linear dependence between the total quantity of tritium occluded and the total surface area. Effusion experiments also indicated similar tri-

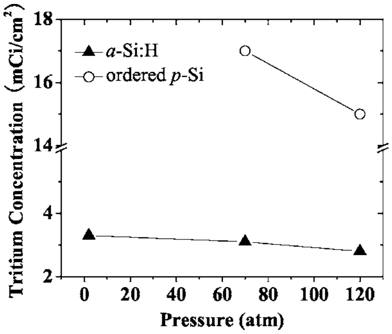

FIG. 4. Concentration of tritium occluded in a-Si:H and ordered p-Si due to T_2 gas exposures at different pressures. In all instances the duration of exposure was 3 days.

tium effusion profiles for DRIE c-Si and p-Si to that obtained for planar c-Si. These results suggest that tritium dispersion and bonding in c-Si samples, irrespective of the surface morphology, are essentially identical. Further, the bonding in c-Si samples is predominantly of the more stable monotritide form, while in a-Si:H samples the dominant form is of the less stable form. With respect to the role of pressure in the tritiation experiments, Fig. 4 shows the tritium content in 300 nm a-Si:H and ordered p-Si samples as a function of T_2 pressure. Tritium incorporation shows little dependence on pressure, suggesting that tritium self-catalysis has a dominant effect on the tritiation of silicon.

Tritium locked in silicon provides potentially a safe and localized on-chip energetic electron source for capacitor charging, particle sensing, molecular excitation and ionization, and micro- to nanopower production. Figure 5 illustrates a simple example of gas ionization using the on-chip tritium high-energy electron source. The ionization current as a function of the applied bias voltage for the various samples is shown. The distance between the electrodes is 1 cm. The saturated ionization current is a measure of the effective surface activity of the tritiated sample.[9] For the saturated current of 40 pA/cm^2 of the c-Si sample, the effective surface activity is estimated to be 0.08 mCi/cm^2, or 80% of total measured tritium concentration. In contrast, the 300 nm tritiated a-Si:H layer yielded an effective surface activity which is only 20% of the total tritium concentration. This is consistent with the average range of 5.7 keV beta particles in silicon being about 0.2 μm.[1] The p-Si sample on the other hand yields an ionization current of 2 nA/cm^2, corresponding to the ratio of the areas of p-Si to planar c-Si samples. Cold electron ionization sources based on tritiated Si are potentially amenable for on-chip microgas or microparticle analyzers. Also, tritiation of p-Si based p-n junctions is a possible configuration of a three-dimensional betavoltaic device.[2]

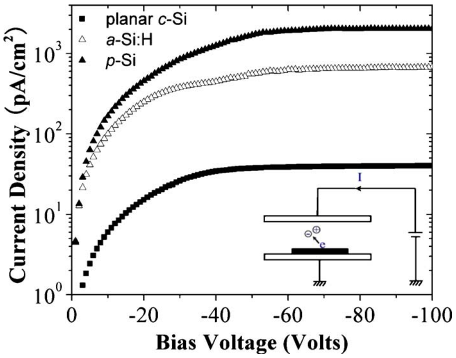

FIG. 5. Ionization current, per unit sample area in air, due to tritiated planar c-Si, a-Si:H, and p-Si as a function of the bias voltage. The gap between the electrodes is 1 cm.

In conclusion, in this work we demonstrate a simple and versatile method to stably incorporate tritium into various types of silicon using T_2 gas. The low temperature posttritiation process described in this letter provides a convenient way to locally integrate a radioisotope micropower source on chip. High-density tritium fuel can be compactly incorporated in textured silicon having an effective surface area of several hundred square meters per cubic centimeter. Tritiated textured Si can be potentially used for luminescence,[3] nanoactuator,[10] particle detector,[11] and voltaic devices.[1,2]

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