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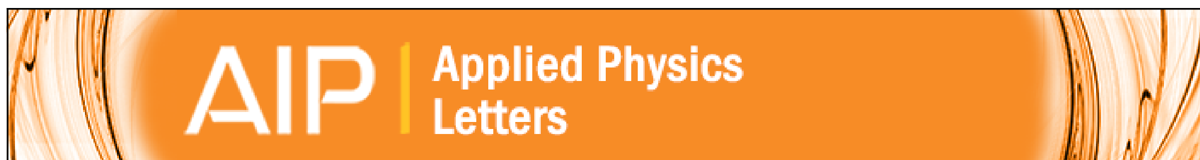

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Tritium locked in silica using 248 nm KrF laser irradiation

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In this Letter we report on selectively occluding tritium in a silica film on a silicon substrate using a combination of high-pressure tritium loading and 248 nm KrF laser irradiation. Sixty percent of tritium dissolved in the silica film was bonded by laser irradiation. The concentration of the bonded tritium was proportional to the total laser fluence. Tritium effusion experiments indicated that the laser-locked tritium existed stably in the glass matrix up to 400 °C. In this work we point a way to a safe and simple approach for the integration of on-chip radioisotope micropower sources for micromechanical and microelectronic applications. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2188384]

Recently there is increasing interest in the development of radioactive isotope micropower sources (RIMS) for self-powered microelectronic and micromechanical devices.[1–3] Tritium is often considered to be an ideal candidate for RIMS applications because it is a pure beta emitter, emits betas of moderate energy, has a relatively long half-life, is safe to handle, and is readily available at a low cost. The principle hurdle to the development of tritium-powered micro-devices has been the need for the incorporation of this radioactive gaseous source with a very limited tolerance for radiation leakage. Consequently, microfabrication techniques for the on-chip integration of high-density tritium have not been extensively investigated.

Hydrogen is used widely in microelectronic and photonic industries. Hydrogen loading is commonly used in fiber Bragg grating writing. First reported by Lemaire *et al.*, the photosensitivity of silica fiber is dramatically enhanced by exposing the fiber to a high-pressure hydrogen environment.[4] The permeated hydrogen molecule reacts with silica under deep ultraviolet (UV) laser irradiation to form a stable -OH bond.[5–7] Hydrogen occluded through this photochemical process increases the UV-induced refractive index change in the silica fiber by four orders of magnitudes.[8] Owing to the increased optical loss in the 1550 nm telecommunication window induced by the -OH bond, deuterium has also been used to red shift the -OH absorption tails beyond 1900 nm.[9] Accelerated thermal annealing tests have shown that -OH bonds formed through UV irradiation are normally very stable up to 400 °C.[8,10] Considering that tritium is chemically identical to hydrogen, notwithstanding the difference in atomic mass and its radioactive nature, it is proposed that similar laser processing can also occlude tritium in glass to provide a stable, on-chip isotope power source.

In this Letter we show that high-pressure tritium loading and deep UV laser irradiation are simple and effective means of occluding tritium in silica glass. By forming the Si-OT bond, the gaseous nuclear fuel is safely immobilized and integrated for on-chip applications. This laser-locking of tritium potentially opens the door to radioisotope micropower on-chip integration for a wide array of microelectronic and MEMS applications.

Tritium loading of silica samples was performed in a custom designed high-pressure, high-temperature tritium glovebox facility. Here, 8 μm thick silica films containing 3% atomic Ge were used. The Ge-doped layer was grown over a 20 μm thick silica-cladding layer on crystalline silicon using the flame hydrolysis deposition technique. This glass composition is widely used in fiber optics. It has high photosensitivity after hydrogen loading.

The loading system consists of a uranium tritide storage bed, an intermediate tritium transfer chamber filled with a molecular sieve, and the sample exposure chamber. The tritium used in each loading experiment was approximately 6000 Ci. The process began by transferring the tritium inventory from the uranium storage bed to the cryogenically cooled (77 K) molecular sieve chamber. The molecular sieve at a liquid nitrogen temperature is capable of adsorbing tritium to densities of 290 Ci/gram at one atmosphere. Upon completion of the transfer of tritium, the molecular sieve and sample exposure chambers were isolated from the storage bed. Next the temperature of both the exposure and molecular sieve chambers were gradually raised to room temperature to release all the tritium and generate a maximum pressure of 6.8 MPa. Subsequent heating of the chambers to 250 °C generates a tritium pressure of about 12.4 MPa. A typical tritium exposure duration ranged from 2 h to 7 days. Following the tritium exposure, the temperature of the system was gradually reduced and the remaining tritium was absorbed by the uranium bed. The samples were transferred from the exposure facility to a liquid nitrogen cooled storage chamber for subsequent experimentation. During this transfer process the samples were exposed to air in a ventilated fume hood for about 15 minutes.

To test the stability of tritium that had permeated into silica glass, effusion measurements were performed on samples that had been tritiated at a tritium pressure of 70 atm

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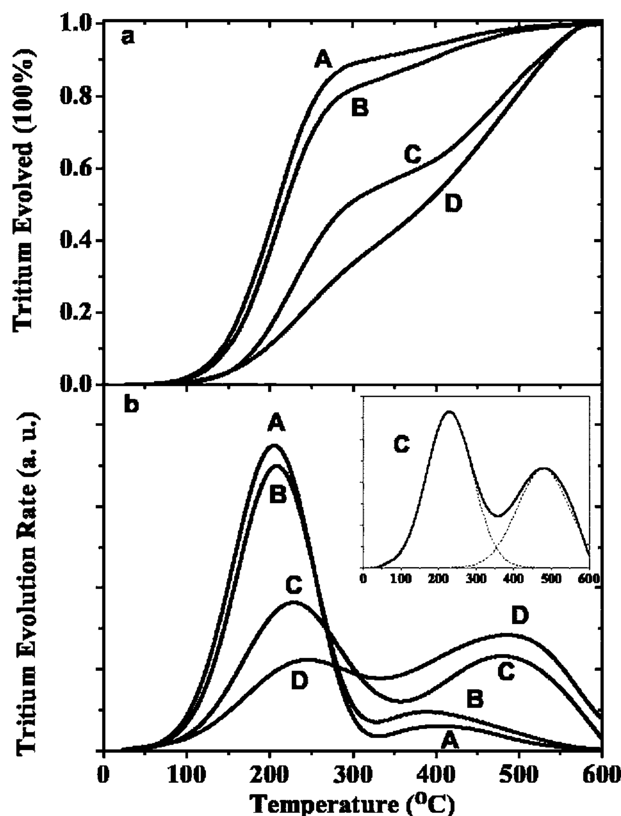

FIG. 1. (a) Total tritium effusion from silica films, and (b) the tritium effusion rate as a function of temperature. The total laser fluence is 0, 700, 3000, 4800 J/cm^2 for traces A, B, C, and D, respectively. The Gaussian deconvolution of trace C is shown as an inset.

and a temperature of 60 °C for 20 h. Immediately after tritium exposure and no laser exposure, a sample was subjected to linear temperature ramping at a ramp rate of 10 °C/min from room temperature to approximately 600 °C in an argon purged tritium effusion monitor.[11] A concentration of 10 mCi/cm^2 was measured, which is equivalent to an estimated tritium atomic concentration of 0.36%. This is much lower than the value reported in hydrogen loading experiments. Lemaire *et al.* have reported 11% atomic concentration of hydrogen can permeate and be subsequently locked in silica fiber. The observed discrepancy is attributed to a lower loading pressure and a shorter loading time. The cumulative tritium evolution is shown in trace A of Fig. 1(a). Most of the tritium effuses out of the sample around 200 °C. The tritium effusion rate as a function of temperature is shown in Fig. 1(b); this is obtained by taking the derivative of the trace in Fig. 1(a). These results show that approximately 90% of the tritium effuses at temperatures below 250 °C with a distinct effusion peak at 240 °C. A smaller effusion peak, ~10% of the tritium, was found at 450 °C. Both peaks are resolved by a Gaussian deconvolution. The low-temperature effusion peak is likely associated with the effusion of molecular tritium trapped in the glass matrix, which has a low activation energy of ~0.4 eV.[12] The high-temperature peak is likely associated with tritium bonded in an-OT hydroxyl form. This supposition is based on similar degradation temperatures (300 °C–400 °C) of most fiber Bragg gratings formed by hydrogenation and 248 nm KrF laser irradiation.[7,8] This suggests that the high-energy beta particles, which have an average energy of 5.7 keV, cause tritium to be self-occluded through beta-induced chemical reactions in the glass matrix.

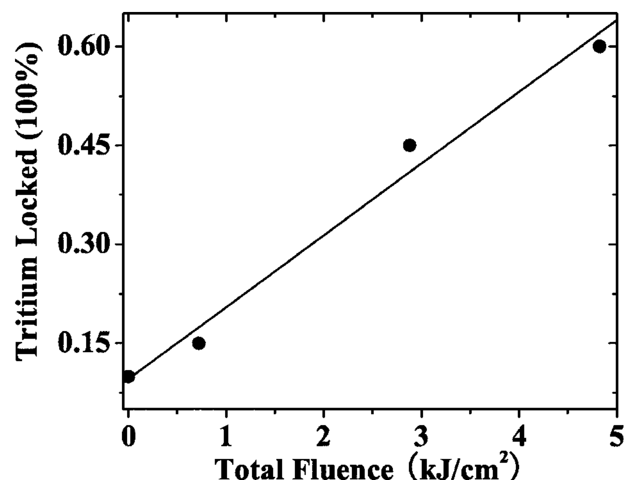

FIG. 2. Percentage of tritium occluded in silica as a function of the total laser fluence.

It is worth noting that the generation of atomic tritium through tritium decay is negligible given its long half-life of 12.3 years. Raman studies to confirm the above have yet to be carried out.

The laser locking experiments were carried out using a 248 nm KrF excimer laser (Lambda Physik Compex 102). The T_2-impregrated samples were irradiated with 20 ns laser pulses at a repetition rate of 20 Hz and a pulse fluence of 20 mJ/cm^2. The effusion results for irradiated samples with 700, 3000, and 4800 J/cm^2 total laser fluence are shown as traces B, C, and D, respectively, in both Figs. 1(a) and 1(b). The effects of laser irradiation are clearly evident in Fig. 1(b), where more tritium is stably bonded and effuses out at higher temperatures (>300 °C). Assuming that the tritium effusing out at 300 °C or higher is stable and chemically bonded tritium, 60% of the permeated tritium is bonded due to laser irradiation at a total fluence of 4800 J/cm^2. This is in contrast to the 10% bonded tritium in nonlaser irradiated samples. Figure 2 shows a linear relationship between the percentage of bonded tritium and the accumulated laser fluence. The nonsaturated relationship suggests that more tritium can be bonded in silica with a further increase in the accumulated laser fluence. The laser locking results presented in this paper are also qualitatively consistent with our

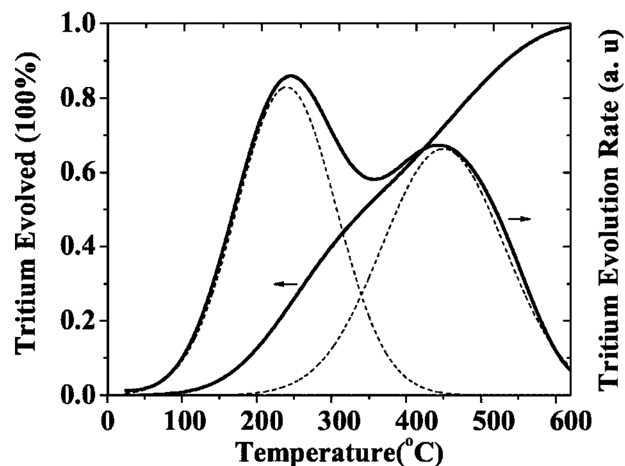

FIG. 3. Tritium effusion from a tritiated silica film stored at room temperature for two weeks post high-pressure tritiation. Gaussian deconvolution of the evolution rate shows two peaks at 240 °C and 450 °C.

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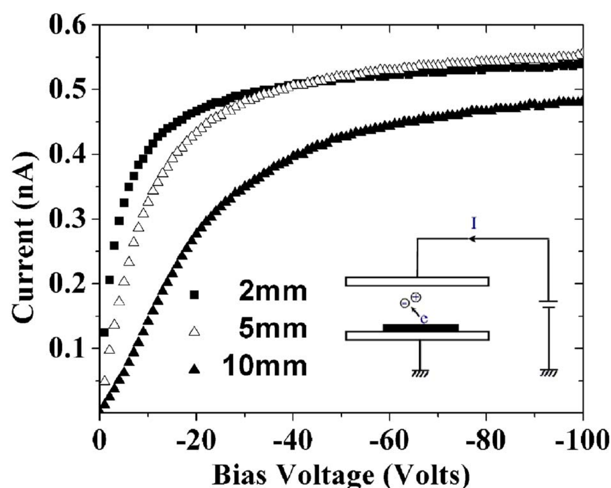

FIG. 4. Ionization current due to a 0.5 cm^2 tritiated silica sample in air as a function of the bias voltage. The air gap is set at 2, 5, and 10 mm.

results of laser irradiation studies in hydrogen-loaded silica fiber of identical composition.[7,8] The accumulated fluence of 4800 J/cm^2 at 248 nm leads to the formation of 0.1 to 0.4 at. % (1000 to 4000 ppm) -OH bonds in hydrogen-loaded 3% Ge-doped silica fiber.[7]

The demonstration of the laser locking of tritium in silica suggests that tritium can be locked on-chip as a micropower source. However, the laser process window is also limited by a "self-locking" process illustrated in trace A of Fig. 1(b). The 20 h tritium loading process has led to 10% tritium locked in a glass matrix without any laser irradiation. This self-locking effect is further manifested in Fig. 3, for a tritiated sample kept at room temperature for two weeks. The effusion measurements revealed a total tritium concentration of 6.3 mCi/cm^2 in the sample, suggesting 37% of the original tritium in the sample outgassed as molecular tritium. For the remaining tritium in silica, the effusion result shown in Fig. 3 indicates that about 30% of the original tritium, in contrast with 10% in trace A, was stably locked and effused out at high temperature. A distinct effusion peak near 450 °C is consistent with effusion peaks formed by the UV laser irradiation, as shown in Fig. 1(b). Figure 3 provides appealing evidence of the formation of -OT bonds, likely catalyzed by high energy electrons from tritium decay.

Tritium locked in silica film provides potentially a safe and localized on-chip energetic electron source for capacitor charging, molecular excitation and ionization, and for micro-nanopower production amenable to a wide array of applications.

Figure 4 illustrates a simple example of molecular ionization using the laser-locked tritium on-chip high-energy electron source. A 0.5 cm^2 tritiated silica film was placed between two metal electrodes with a potential difference applied by an external voltage source. High-energy electrons emitted by on-chip tritium ionize the ambient gas molecules and thus result in the measured ionization current. Figure 4 shows the ionization current as a function of the applied bias voltage for three different electrode-gap distances of 2, 5, and 10 mm. It is interesting to note that the saturated ionization current is a measure of the effective surface activity of the tritiated sample.[13] For the saturated current of 500 pA shown in Fig. 4, the effective surface activity is estimated to be 1 mCi/cm^2 in contrast to the total tritium dosage of 10 mCi/cm^2 in the 8 μm glass films. This is due to the short range of beta particles in solids; in silica the average and maximum range are 0.4 and 2 μm, respectively.[14] Such on-chip ionization sources could be useful for on-chip microgas or micro-particle analyzers.

The laser locking of tritium presented in this Letter offers an intriguing approach to nuclear micro-engineering for on-chip applications. Through the combination of photolithography masking and localized laser irradiation, the isotope can be selectively locked in silica glass films in a stable -OT form. Also, unreacted molecular tritium can be readily desorbed by thermal annealing at 300 °C. Tritium micropower sources at the micron scale could be monolithically integrated on chip with microelectronic circuits, MEMS units, and microfluidic devices for a wide array of applications.

In conclusion, in this Letter we report on the selective laser locking of tritium on-chip. Using 248 nm KrF laser irradiation, 60% tritium has been stably locked in silica films on silicon substrates. Effusion experiments indicate that laser-locked tritium is stable up to 400 °C in contrast to an effusion temperature of 200 °C for tritiated samples without laser treatment. This work demonstrates a safe and simple approach to integrate radioactive micropower sources on-chip for MEMS and micro-electronics applications.

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