Electrolytic fabrication of atomic clock cells

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We describe an electrolytic method to release controlled amounts of free alkali metal into miniature cells in a silicon wafer with anodically bonded glass windows. © 2006 American Institute of *Physics.* [DOI: 10.1063/1.2219730]

There is considerable current interest in developing very small frequency standards and magnetometers, based on magnetic resonances in optically pumped K, Rb, or Cs vapors. It is hoped that these could be mass produced at a cost, size, and power requirement that would permit wider applications. In the chip scale atomic clock (CSAC) program of DARPA, the most common approach has been to manufacture miniature cells by anodically bonding¹ glass wafers to both sides of a silicon wafer, containing many small holes. Each of these small holes is destined to be a vapor cell. Many hundreds of cells can be mass produced on a single silicon wafer. Each cell must be integrated with a vertical cavity surface emitting laser (VCSEL), a photodetector, electronics, a thermal control system, etc.

At the present time, three methods have been used to fill the anodically bonded cells with Rb or Cs metal. The most straightforward method^{2,3} is to inject a small amount of liquid Cs or Rb metal into the cell, along with an appropriate mixture and pressure of buffer gases, directly before it is sealed. The hole is then hermetically sealed. The second method⁴ is to manufacture each small cell with mixture of alkali-metal salt and reducing agents that can release the required Cs or Rb metal into the cell after appropriate thermal processing. The third method⁵ makes use of enclosed alkali metals in a chemically inert wax to preform alkali metal-wax micropackets. Then the micropacket is attached to the silicon nitride membrane side of a cavity and the enclosed alkali metal is released into the cavity by laser ablating the silicon nitride membrane through the other glass wafer side of the cavity.

In this article we describe a new electrolytic method to fill cells. It is relatively simple, it permits good control of the amount of metal released in the cells, and it lends itself to mass production with silicon wafers. Here we discuss Cs, but cells can be filled with the other alkali metals, e.g, Rb, K, and Na, in an analogous way. The method is based on the fact that large amounts of alkali metal can be released by passing an electrolytic current through hot glass.⁶

The steps of a proof-of-principle experiment to illustrate electrolytic cell filling are shown in Fig. 1. A simple, cesiumenriched glass was made by melting a mixture of cesium carbonate and boron oxide at 900 °C for 30 min. The resulting molten glass was slowly cooled to room temperature. A hole, 2.5 mm in diameter, was drilled through a $\langle 100 \rangle$ silicon wafer, with a thickness of 2.5 mm, and polished on both sides. The wafer was *p* doped and had a resistivity $\geq 1 \Omega \text{ cm}^2$. For mass production, holes could be made with photolithographic patterning, selective chemical etching, deep reactive ion etching, etc. A shallow well, 2.5 mm in diameter, was drilled into the surface of a Pyrex wafer, 3 mm in thickness, to contain Cs glass. As sketched in Fig. 1(a), the silicon wafer (gray) and the Pyrex wafer (light blue) with fragments of Cs-enriched glass (dark blue) in the well were pressed against a graphite disk (not shown) and anodically bonded by heating the assembly on a hot plate to 500 °C and applying a potential difference of +1000 V between the silicon and the graphite.

A second Pyrex wafer was anodically bonded to the other surface of the silicon wafer to make a sealed cell, as shown in Fig. 1(b). For simplicity, the anodic bond was formed under an argon cover gas, so the newly manufactured cell contained nearly pure argon gas at a room-temperature pressure of 0.4 atm. For clock applications, appropriate mixtures of argon with nitrogen gas can be used to diminish the sensitivity of the clock frequency to temperature fluctuations^{7,8} and to suppress radiation trapping. The newly sealed assembly was heated with a gas flame to melt the cesium-enriched glass and make good contact with the Pyrex substrate. Our simple Cs glass had a much larger coefficient of thermal expansion than Pyrex so a network of cracks developed in the Cs glass when the assembly cooled. To maintain a window with good optical quality, the Cs-glass well was displaced from the hole in the silicon by about 2 mm, so most of the cell window was not obscured by the crazed Cs glass. The final cell consisted of a three-layered bonded structure with optically transparent Pyrex windows on either side of the hole in the silicon.

As sketched in Fig. 1(c) an "ion anode" was constructed from a copper stem. A small basin at the top of the stem contained molten NaNO₃ salt. The anode was centered under the Cs glass. The bottom of the stem was attached to a massive copper base, resting on a hot plate. NaNO₃, which melts at 307 °C, provided Na⁺ ions for injection into the glass. The temperature of the hot plate was set at 540 °C and we waited a few minutes for thermal equilibrium to be established. Then we turned on the high voltage power supply and increased the voltage gradually to 700 V. The current, monitored with a meter in the circuit, was several milliamperes and was quite stable. The electrolysis was done for several minutes, sufficient time for a film of yellow Cs metal to form on the top window of the cell and to coalesce into droplets. This is much more Cs metal than would be needed or desired in practice. When the cell cooled, much of the Cs metal recondensed on the silicon sidewalls of the cell. Several such



FIG. 1. (Color online) Schematic of the experimental process. (a) A silicon wafer with a hole of 2.5 mm in diameter was anodically bonded to a Pyrex wafer with a shallow well, 2.5 mm in diameter. Pieces of Cs-enriched glass (darker blue) were melted into the well. (b) Another Pyrex wafer was anodically bonded to the other free surface of the silicon wafer under an argon cover gas. (c) A copper stem, containing molten NaNO₃ salt in a basin at the top, was pressed against the Pyrex below the Cs-glass well. The stem was attached to a copper base, resting on a hot plate at a temperature of 500 °C. A potential of +700 V was applied for a few minutes between the molten NaNO₃ andee and the silicon cathode.

cells have been made successfully with this electrolytic method so it is reproducible. A photograph of the top of one of the cells is shown in Fig. 2.

It is important that most of the electrolytic current be used to reduce Cs^+ ions to Cs atoms in the cell, and that the concomitant reduction of Na⁺ ions to Na atoms in the anodic bond be minimized. The bond can be ruined if too many Na atoms are reduced there.^{9,10} In these first experiments, two methods were used to guide most of the current to the Cs glass: (1) the current was localized by using a small-diameter ion anode, and (2) the molten salt provided good thermal contact to the glass and permitted us to keep the Pyrex above the anode hotter and more highly conducting than for the surrounding Pyrex glass.

In Fig. 3 we show calculated current distributions from a circular ion anode, through a glass plate, to a silicon cathode. We assumed constant conductivity σ in the glass and a current density $\mathbf{j}=-\sigma\nabla\phi$, where ϕ is the electrostatic potential. We found $\phi=\phi(r,z)$ as the axially symmetric solution to Laplace's equation $\nabla^2\phi=0$ in cylindrical coordinates r, θ, z . The coordinate system is centered on the ion anode. At the bottom of the glass plate z=0; at the top, z=d. The boundary conditions were $\phi=0$ for the glass-silicon interface at the top and $\phi=V$ at the glass-salt interface. We assumed no current flow into glass except through the salt, so for the parts of the



FIG. 2. (Color online) Photograph of the top surface of the cell with golden metal inside.



FIG. 3. (Color online) Distribution of current from an ion anode to a silicon cathode through a glass plate. The horizontal coordinate is the distance from the center of the glass. The vertical coordinate is the height from the bottom of the glass. Both distances are given in units of the plate thickness d. (a) The diameter of the ion anode is 8d. (b) The diameter of the ion anode is d. (c) The diameter of the ion anode is negligibly small compared to d.

bottom surface that were not in contact with the salt we set $\partial \phi / \partial z = 0$. The labels 0.1,...,0.9 indicate surfaces of revolution containing fractions 0.1,...,0.9 of the electrolytic current. As shown in Fig. 3(a), when the diameter of the anode is much larger than the glass thickness, most of the current flows to a cathode area that is only slightly larger than the anode area. The current collection area on the cathode can be diminished by diminishing the diameter of the ion anode. Figure 3(b) shows the current flow for an anode with a diameter equal to the glass thickness. Figure 3(c) shows that the collection area for a "point-source" anode is only slightly smaller than that of the finite anode of Fig. 3(b). As mentioned above, there will be further concentration of the current because of higher conductivity of the hot glass above the anode. This calculation is a simplified model of how the decrease of the ion anode's size can help concentrate the electrolysis current. In the real case, the glass consists of two parts. One is the Cs-enriched borate glass with higher conductivity and the other is the Pyrex glass with lower conductivity. The higher conductivity of the Cs-enriched borate glass can help concentrate the current even more than the calculated result. Since the current is concentrated into the Cs-enriched borate glass, most of the reduced metal is Cs rather than Na. The total number of metal atoms is equal to the time integral of the current divided by the elementary charge e.

To prove that there was free Cs metal in the cells made with this method, we measured the absorption of Cs resonance light generated by an external-cavity, single-mode diode laser (Toptica DL100). The laser frequency was tuned to the peak of the D1 resonance line of cesium. We measured the peak absorption of the cell for temperatures ranging from 90 to 130 °C. The power of the transmitted light was measured with a photodiode. Let *I* be the intensity of the transmitted light when laser frequency is tuned to peak absorption, and let I_0 be the intensity of the transmitted light when there is no resonant absorption of the light from the vapor, in our case, when the cell is at room temperature and vapor density is too small to cause significant absorption. Then the number density of the alkali-metal atoms in the cell is



FIG. 4. (Color online) Number density of cesium atoms in our Cs cell (red solid dots) and the standard number density of the Cs vapor which is in thermal equilibrium with metal (blue curve).

$$N = \frac{\ln(I_0/I)}{\sigma L}.$$
(1)

Here L=0.25 cm is the length of vapor through which the laser beam passes. The peak absorption cross section,¹¹ $\sigma=4.0 \times 10^{-13}$ cm², for Cs atoms in 0.4 amagat of Ar is nearly independent of temperature. All the cells have been measured and all of them have Cs inside. One of the results of these measurements is shown as points in Fig. 4. The continuous curve is the number density of Cs vapor in equilibrium with pure liquid Cs as tabulated by Nesmeyanov.¹² The density of Cs vapor in the electrolytically filled cell is very nearly equal to the saturated number density.

The electrolytically filled cells could be optically pumped very well. For example, a microwave end resonance¹³ from one of the cells is shown in Fig. 5. The cell was pumped with 7.6 mW/cm² of circularly polarized light from the same diode laser used to make the density measurements of Fig. 4. The transmitted light was measured with a photodiode. The microwaves came from a horn antenna.

Straightforward extensions and improvements of the proof-of-principle experiments described here would make it possible to fabricate and fill many cells in parallel on a single wafer assembly.



FIG. 5. (Color online) Microwave end resonance. The full width at half maximum is 12.3 kHz; on resonance the transmission decreased by 16.7%, the resonance frequency was 9.193 14 GHz, the static field was 0.13 G, and the temperature was 110 $^{\circ}$ C.

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