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BRIEF REPORTS AND COMMENTS

This section is intended for the publication of (1) brief reports which do not require the formal structure of regular journal articles, and (2) comments on items previously published in the journal.

Versatile Rb vapor cells with long lifetimes

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The authors report on an approach to the construction of long-lasting rubidium atomic vapor cells. The method uses pinch-off copper cold-welds, low temperature solders, and electroplated copper to create long-lasting hermetic seals between containment chambers of dissimilar geometries and materials. High temperature epoxy, eutectic lead/tin solder, and indium solder were considered as sealing materials. These seals were analyzed using accelerated lifetime testing techniques. Vapor cells with epoxy and bare metal solder seals had a decrease in the rubidium atomic density within days after being heated to elevated temperatures. They also exhibited broadened spectra as a result of rubidium reacting with the seals. However, indium solder seals with a passivation coating of electroplated copper did not exhibit a significant decrease in linewidth or atomic density after being held at 95 °C for 30 days. The authors conclude that this particular seal has no rubidium chemical reaction failure mode and when used in combination with copper cold welding has the potential to create multiplatform vapor cells with extremely long lifetimes. © *2013 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4795759]

I. INTRODUCTION

Alkali vapor cells are used in a number of device-oriented applications. Examples include atomic clocks,[1] communication system switches and buffers,[2] single photon generators and detectors,[3] gas phase sensors,[4] nonlinear frequency generators,[5] and precision spectroscopy instrumentation.[6] Historically vapor cell construction has relied on high temperature glass forming and sealing. In order to broaden the potential application of vapor cells, however, we need them to be scalable, versatile, long-lasting, and suitable for packaging with nonflat geometries and mixed materials. Such cells could be incorporated into many systems to help reduce cost and improve integration with optical elements made using standard microfabrication processes. Several alternate packaging techniques have been explored to satisfy these requirements,[7–10] including a previously reported rubidium (Rb) vapor cell formed using epoxies and cold welding.[11]

While the vapor cell construction techniques described here are designed to accommodate a wide variety of end applications, they are driven by the desire to integrate Rb cells with hollow waveguides on silicon chips.[12] Successful introduction and sealing of Rb in this waveguide platform entails multiple requirements for vapor cell construction:

(1) We must be able to evacuate the cell to an optimal pressure (which may differ for each application).
(2) No materials used can chemically react with Rb.
(3) The seal must be long lasting, as the cell will be irreplaceably attached to the platform.
(4) The cell must be able to withstand normal operating AND fabrication temperatures.
(5) The construction technique must allow for sealing of dissimilar materials with nonplanar geometries.
(6) The cell must be on the same order of size as a chip-scale platform so as to minimize pressure and stress during handling.

The first three of these requirements are met with most traditional fabrication methods, but the last three exclude all but the cold weld technique[11] for vapor cells with fragile and complex geometries. The basic idea behind this approach involves attaching one end of a copper (Cu) cylinder to the body of a glass-based containment vessel suitable for spectroscopy. Solid Rb is placed in the reservoir and a vacuum is attached to the open end of the copper cylinder, evacuating the device to the desired pressure (~1 mTorr for most spectroscopy experiments). Copper pinch-off pliers are then used

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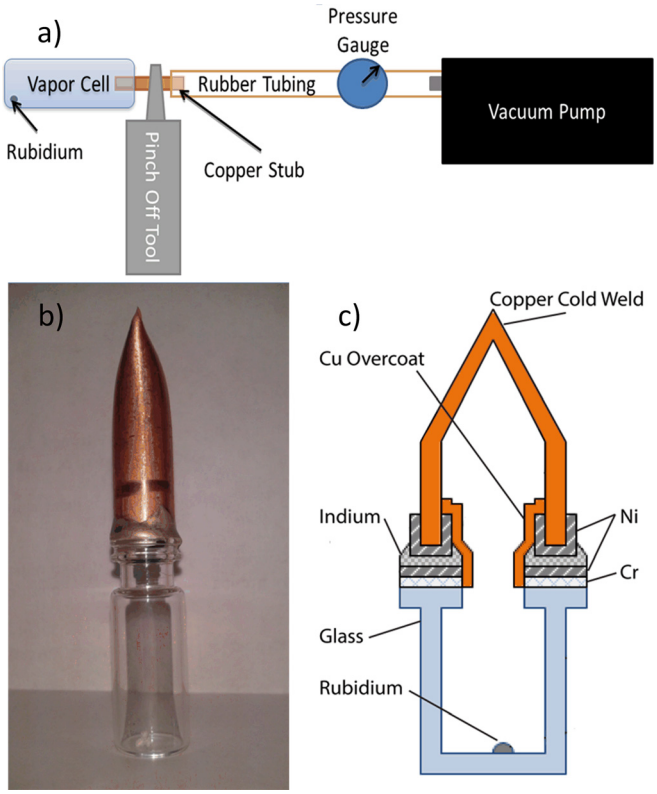

FIG. 1. (Color online) (a) Cold-weld sealing with copper crimping and vacuum setup. (b) Photograph and (c) cutaway illustration of a minicell with copper plated indium solder seal.

to create a cold-weld seal in the copper cylinder and separate the cell from the vacuum system [see Fig. 1(a)]. The Rb loading procedure must be done in a glovebox with an inert nitrogen or helium atmosphere since Rb is highly reactive with oxygen and water. Copper was chosen as the reservoir since its pliability allows for excellent hermetic seals with cold-weld pinch off pliers,[13] and it has been shown to be compatible with Rb.[11] The material used to join the copper reservoir to the transparent vapor cell body, if the technique is to be truly versatile, must have the ability to wick and fill in voids allowing for a gentle attachment of two surfaces with dissimilar and potentially nonflat geometries.

In the first report of the cold-weld methodology,[11] a high temperature epoxy was used as the sealing material between the copper reservoir and the vapor cell body. This technique was successful in creating viable Rb vapor cells on two dissimilar platforms: macrosized minicells and microsized chips. The Rb absorption spectrum, electromagnetically induced transparency, and slow light were all successfully observed utilizing this technique.[12,14,15] The main drawback of this method was the limited durability of the seal between the copper and vapor cell body. Accelerated lifetime tests showed that the epoxy had an adverse reaction with the Rb, slowly causing cells to fail at the elevated temperatures necessary to produce high optical densities in the cell. It was determined that for the epoxy seal, the expected lifetime was around three days when heated to 90 °C. Here, we document a suitable replacement for the epoxy seal that keeps many of its benefits (versatility and gentleness) while dramatically increasing device longevity.

II. METHODOLOGY

After an exhaustive investigation into available epoxy adhesives without achieving long-term sealing success, other sealing materials were considered. Rubidium has previously been shown to be compatible with glass and copper over long periods at elevated temperatures in cells created using "Houskeeper" seals.[11] Houskeeper seals use a compression technique to join a glass cylinder around a copper one.[16] Using the Houskeeper technique is not a versatile packaging solution because it requires specific geometries, high heat, and the ability of the materials to withstand high stresses. However, it does point a way toward satisfying requirements for a long lasting sealing approach: limit Rb exposure to only glass and copper. This could potentially be achieved by creating a metallic(solder) seal between the copper reservoir and the glass vapor cell surface and then coating the solder with copper via electroplating. Low temperature solders are ideal since many integrated platforms may be sensitive to high temperatures. Two solders were investigated in this study—eutectic tin/lead(Sn/Pb), which melts at 183 °C, and pure indium(In), which melts at 157 °C. The Sn/Pb solder was chosen due to its excellent wettability to copper and ubiquitous nature in the electronics industry. Indium was chosen for its ultralow melting temperature and relatively high malleability.

The use of solder as a seal requires a solderable surface on silicon dioxide (glass). In these studies, this is achieved by evaporating a 250 nm layer of chromium (Cr) followed by a 250 nm layer of nickel (Ni) onto the glass surface. The chromium/nickel layer acts as a "seed" metal surface over which an additional 3 μm of nickel is electroplated. Since indium and copper form a brittle intermetallic, 3 μm of nickel is also electroplated on the base of the copper cylinder where it contacts solder when a seal is formed. This takes place when the vapor cell and copper reservoir are heated to 200 °C, cleaned with a water-soluble flux, and then joined together with solder. The cell is then cleaned by rinsing with deionized (DI) water, followed by a 15 min soak in 55 °C acetone, an isopropanol rinse, a 5 s dip in 48% hydrofluoric acid, and finally another DI water rinse.

Having cleaned off all of the flux and oxides created during the soldering process, 3 μm of copper is electroplated over the soldered joint. This is done by attaching the cathode to the copper reservoir, placing a pure copper wire into the center of the cell to act as the anode, and flowing copper electroplating solution through the vapor cell while passing a current from the anode to the cathode. The electroplating solution is created on-site using DI water mixed with 225 g/L of copper sulfate ($CuSO_4$-$5H_2O$) and 65 g/L of sulfuric acid (H_2SO_4). The electroplating process is conducted at room temperature using a potentiostat to supply current at a density of 4.6 A/dm^2. The electroplated layer of copper is referred to as the Cu overcoat.

After electroplating, the cell is again rinsed with DI water, dipped in 48% hydrofluoric acid for 5 s, again rinsed

with water, rinsed with isopropanol, and then placed in a 120 °C dehydration oven for 2 h. Figures 1(b) and 1(c) illustrate the final form of a copper coated indium vapor cell (termed a minicell) made using 3/8 in. copper pipe and a glass chromatography bottle. The cells are loaded with Rb, evacuated to a pressure of 1 mTorr, and copper cold welded in a nitrogen filled glovebox as previously described.[11]

III. EXPERIMENTS AND RESULTS

Vapor cells were evaluated by monitoring the Rb spectral absorption peaks and their Voigt profile FWHM linewidths[17] in high temperature, accelerated lifetime tests. Specifically, optical transitions of the D2 lines in natural rubidium ($5^2S_{1/2} \rightarrow 5^2P_{3/2}$) were monitored using a tunable laser swept over a ~12 GHz range centered around 780.24 nm.[14] All optical tests took place when the cells were heated to 46 °C, although they were stored for long periods at higher temperatures.

Experimental measurements were compared to a theoretical model, which takes into account the two isotopes of natural occurring Rb, all hyperfine energy transitions, Doppler broadening, and collisional and pressure broadening.[18,19] This theoretical model was used to extract the atomic density and homogeneous linewidth via a least squares fit.

The spectrum in Fig. 2(a) shows experimental points plotted with a fitted theoretical curve for an epoxy sealed minicell that had been stored at 95 °C for 15.5 days. To fit the measured points, the theoretical model had to include significant pressure broadening yielding a homogeneous linewidth of (1046.00 ± 15.13) MHz. This is magnitudes of order higher than the ideal theoretical value of ~6 MHz. It should also be noted that the linewidth continues to grow until the spectral signal disappears completely due to the total elimination of Rb vapor. This indicates either a leak in the seal or the existence of a gaseous by-product from a chemical reaction. The atomic density for this cell is calculated to be $(5.01 \pm 0.33) \times 10^{10}\,\mathrm{cm}^{-3}$, which is much lower than the theoretical value of $7.37 \times 10^{10}\,\mathrm{cm}^{-3}$. This indicates that the Rb was reacting with some material in the cell, reducing the overall concentration of Rb.

Figure 2(b) shows a spectrum for a minicell made using an indium solder and Cu overcoat. The experimental points were gathered from optical tests performed at 46 °C after the minicell had been stored at 95 °C for 33 days. Based on the data gathered and the complete theoretical model, the spectrum yielded a homogeneous linewidth of (55.56 ± 24.69) MHz and an atomic density of $(7.41 \pm 0.16) \times 10^{10}\,\mathrm{cm}^{-3}$, which matches the theoretical value of $7.37 \times 10^{10}\,\mathrm{cm}^{-3}$. The relatively small increase in the homogeneous linewidth was present in the cell at time zero. This initial increase in linewidth is caused by the outgassing of contaminants embedded in the glass walls during the fabrication process. Though the cleaning process outlined in this paper is the best-known-method, the large surface areas and porous nature of glass has kept us from thus far eliminating the contamination completely. Research to overcome this problem is ongoing. Since the atomic density is at theoretical levels and the initial linewidth does not increase during the entire duration of the month long test at elevated temperatures, the seal itself is considered to not have a fail mode.

Minicells with bare Sn/Pb and indium solders were tested along with cells with Cu overcoats. A batch of minicells sealed with Aremco 2310 epoxy (similar to those utilized in

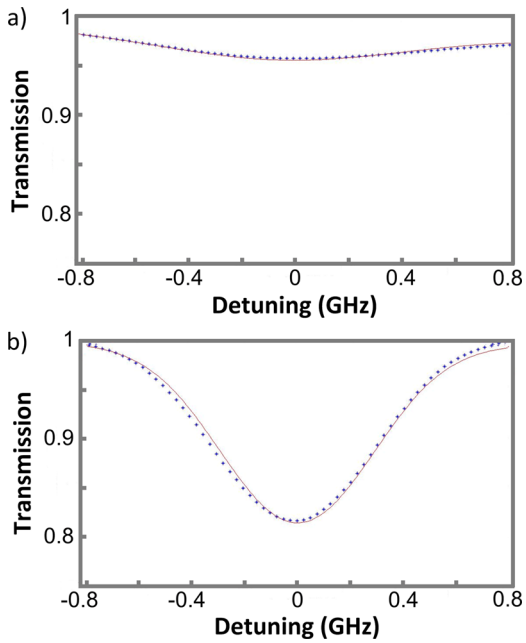

FIG. 2. (Color online) Experimental (blue stars) vs theoretical spectrum (purple solid line) of the ^{87}Rb F = 1 transition for (a) a "dying" epoxy minicell and (b) a long-lasting copper-coated indium minicell. The residual sum of squares are 4.37×10^{-4} and 1.33×10^{-3} for (a) and (b), respectively. The main source of error in these fits is due to vapor cell temperature monitoring limitations in our system.

a)

		Type of Seal				
		E	Sn/Pb	In	Cu-Sn/Pb	Cu-In
Temperature	95 °C	3.6	1.6	0.5	1.6	N/A
	80 °C	6.4	2	3.7		
	65 °C	15.2	5.8	5.6		
		Time to Failure (Days)				

b)

	Type of Seal		
	E	Sn/Pb	In
E_a (J/mol)	0.52	0.47	0.87
A (s^{-1})	3.91×10^5	1.95×10^6	1.37×10^{12}

FIG. 3. (a) Observed days to failure (average) for tested minicells by material type [epoxy(E), Sn/Pb, In, Cu plated Sn/Pb(Cu-Sn/Pb), and Cu plated In(Cu-In)] and temperature. (b) E_a and A constants [see Eq. (1)] for minicells with measureable failure times.

the previous study,[11] but with dimensions and Rb volumes equal to those in the soldered cells) were also tested. These tests were done in order to compare the improvement of solder to epoxy seals.

Predictive lifetime studies were made by testing three or more minicells of each type (epoxy, Sn/Pb, indium, copper coated indium, and copper coated Sn/Pb) stored at the following temperatures: 65, 80, and 95 °C. The optical depth and FWHM linewidth of the combined Voigt profiles in the D2 ^{85}Rb $5^2S_{1/2}$ (F = 3) → $5^2P_{3/2}$ (F = 2,3,4) absorption peak were monitored at least once a day until failure. Since a drop in the optical depth can be caused by both a drop in the atomic density and pressure broadening, failure of a cell was defined as a 30% drop in the peak absorption depth of the D2 line transition. The collected failure data (average failure times for the minicells of each time stored at each temperature) can be viewed in Fig. 3.

A modified version of the Arrhenius equation was used to predict lifetime and is shown as[20,21]

$$\ln(k) = \ln(1/t) = -E_a/R * (1/T) + \ln(A), \quad (1)$$

where k is the process rate, E_a is the activation energy, T is the temperature, R is the gas constant, and A is a constant. For our experiments, we monitored catastrophic failure; therefore, the reaction rate, k, can be simplified to $1/t$, where t is the time it takes for the device to fail. Equation (1) becomes a linear relationship with respect to $\ln(1/t)$ and $1/T$. By fitting a line to the empirically gathered data from the accelerated lifetime tests, t being days to failure and T being the temperature, we can solve for E_a and A. Using Eq. (1) and solving for t, we can then obtain the expected lifetime of the devices at any temperature. These experiments predict a room temperature device lifetime of 161 days for epoxy, 45 days for bare Sn/Pb, and 413 days for bare indium. The goodness-of-fit values (R^2) between the gathered data and the lifetime estimates are 0.99, 0.90, and 0.85 for epoxy, bare Sn/Pb, and bare indium, respectively.

All the copper coated solder minicells were stored at 95 °C. Testing was halted for the copper coated Sn/Pb minicells since they appeared to be suffering from poor copper adhesion and their failure when stored at 95 °C was identical to the uncoated Sn/Pb minicells. This seemed to indicate that Rb was penetrating beneath the Cu overcoat and reacting with the underlying Sn/Pb solder. However, the copper plated indium seals were observed to last for over 30 days at 95 °C with no degradation in atomic density and no peak broadening. Since failure times could not be obtained at this temperature, it was assumed failure times would not be found at lower temperatures and so these tests were not performed.

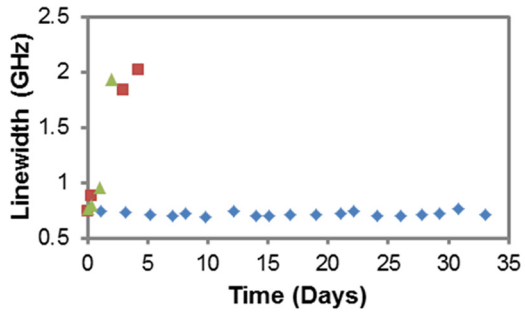

FIG. 4. (Color online) Voigt profile FWHM linewidth vs time for copper plated indium (blue diamonds), epoxy (red squares), and lead-tin (green triangles) minicells. These minicells were stored at 95 °C and optically tested at 46 °C.

It is important to note the evolution of the pressure and Doppler broadened spectral linewidth during the experiments. For the bare indium and copper-plated indium minicells, no noticeable increase in the linewidth occurred. However, for the epoxy and the Sn/Pb minicells, the linewidth did increase leading to the eventual merging of all four absorption dips in the Doppler broadened Rb D2 lines.

Figure 4 compares the typical spectral linewidth response for epoxy, bare Sn/Pb, and Cu coated indium minicells. As mentioned earlier, this increase in the spectral linewidth is likely due to a gaseous byproduct between the Rb and sealing material or, in the case of the epoxy, the outgassing of solvents, water, or carbon dioxide, a common occurrence for epoxies, even certified low-outgassing versions.

IV. SUMMARY AND CONCLUSIONS

After observing that Rb vapor cells created with copper-plated indium solder maintain high atomic densities at 95 °C for over 30 days, we conclude that this method has no rubidium chemical reaction failure mode, resulting in vapor cells with extremely long lifetimes. The sealing technique builds upon our previous success with the copper cold-weld sealed reservoir and adds a Rb neutral passivation coating over an indium seal. Due to the gentle nature of the indium solder process, we submit that the indium-copper combination provides the most versatility in packaging, especially when considering the drive to miniaturize vapor cell technologies.

The Sn/Pb solder seal, via the fabrication method described in this paper, did not exhibit good copper electroplating properties. Though possible alterations to the copper plating process could improve the plating adhesion, ultimately it was decided to abandon Sn/Pb solder since we found the joints to be highly stressed which resulted in a high rate of structural failure in our devices. Vapor cells with geometries and materials better suited to stressed joints could potentially create long lasting minicells with Sn/Pb solder using a technique similar to the one outlined in this paper. However, we submit indium as a more versatile sealing option due to its relatively malleable nature that allows for low stress joints making it acceptable to a wider array of materials and geometries.

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