Wafer-level filling of microfabricated atomic vapor cells based on thin-film deposition and photolysis of cesium azide

Li-Anne Liew[a] and John Moreland
Electromagnetics Division, National Institute of Standards and Technology, Boulder, Colorado 80305

Vladislav Gerginov
Time and Frequency Division, National Institute of Standards and Technology, Boulder, Colorado 80305

(Received 22 December 2006; accepted 1 February 2007; published online 15 March 2007)

The thin-film deposition and photodecomposition of cesium azide are demonstrated and used to fill arrays of miniaturized atomic resonance cells with cesium and nitrogen buffer gas for chip-scale atomic-based instruments. Arrays of silicon cells are batch fabricated on wafers into which cesium azide is deposited by vacuum thermal evaporation. After vacuum sealing, the cells are irradiated with ultraviolet radiation, causing the azide to photodissociate into pure cesium and nitrogen *in situ*. This technology integrates the vapor-cell fabrication and filling procedures into one continuous and wafer-level parallel process, and results in cells that are optically transparent and chemically pure.
[DOI: 10.1063/1.2712501]

The recent application of microelectromechanical system (MEMS) technology to atomic-based instruments has inspired development of various chip-scale atomic devices (CSADs) including clocks[1,2] and magnetometers.[3] Central to CSAD technology are microfabricated alkali vapor cells[4] for containing cesium or rubidium vapor and buffer gases. Several techniques have been developed for cell microfabrication.[1–7] Whereas conventional vapor cells for larger-scaled atomic devices are made by glass blowing, those made by microfabrication technology most commonly take the form of small holes or cavities etched in silicon wafers and sealed with glass windows.[4] The empty cells are easily batch fabricated in a clean room using techniques common to MEMS fabrication such as photolithography, silicon etching, and anodic bonding; however, the critical step remaining is to fill the empty cell with cesium or rubidium and buffer gases. Cell filling has developed as an entirely separate endeavor from cell fabrication, and one that poses an ongoing MEMS packaging challenge. Difficulties are encountered in manipulating the highly volatile alkali metals in a wafer-compatible scheme, as well as the fact that the high temperatures needed for silicon-to-glass anodic bonding (which is needed to hermetically seal the cell) are at odds with the low melting points of cesium and rubidium.

Our previous approaches to cell filling involved pipetting liquid cesium into the cell cavity in an anaerobic glovebox[4] or reacting chemical precursors to produce the pure alkali metal in ultrahigh vacuum either in the cell itself[4] or in an ampoule followed by diffusing the alkali metal into the cell cavity.[5] Other researchers have developed filling methods based on transferring liquid rubidium in microfluidic channels[6] or pipetting rubidium into wax packets in a glovebox followed by laser ablation to release the rubidium into the cell.[7] While each method has its strengths, a common drawback is the need for microfluidic manipulation of the liquid cesium or rubidium. Not only is this technically challenging as alkali metals are highly volatile, this also limits the filling procedure to a sequential rather than parallel process or may introduce nonalkali chemical residues into the cell which could affect the chemical stability within the cell. These drawbacks may in turn lead to variability from one cell to another, affect the performance of the cell, or may be cost prohibitive for commercialization.

To address these challenges, we describe a cesium batch-filling technique based on thin-film deposition and decomposition of cesium azide (CsN_3). CsN_3 is a solid at room temperature and is stable in air, and decomposes to produce pure cesium and nitrogen gas when heated to 450 °C or, as we have found, when exposed to ultraviolet (UV) radiation. The CsN_3 method of cell filling eliminates the need for fluidic manipulation of pure alkali metals, thus greatly simplifying the filling process. Thin-film deposition is compatible with traditional wafer-scale fabrication processes and thus has the potential to be highly scalable. However, due to the relative lack of published experimental data on this compound, much of this work has been exploratory in nature. Concurrent to our efforts, Ogden *et al.*[8] recently demonstrated, using a matrix isolation technique, that solid CsN_3 can be heated and vaporized *in vacuo* in the presence of a matrix host gas (Ar or N_2) and then cocondensed with an excess of the matrix host onto a CsI window that was cooled to 12 K. The objective of our research was to deposit films of CsN_3 onto silicon or glass substrates by the use of standard vacuum thermal evaporation in order to develop a wafer-compatible process.

Figure 1(a) shows the design of a single cell, as described in our previous publication.[4] The internal cavity is typically about 1 mm wide but may be varied from a few micrometers to millimeters. Arrays of cells were fabricated, filled, and sealed in parallel in the process shown in Fig. 1(b). The starting material was a 1-mm-thick, double-sided polished ⟨100⟩ silicon wafer. Arrays of square holes were simultaneously etched through the wafer from both sides using KOH solution or deep reactive ion etching. Pyrex wafers, 125 μm thick, were anodically bonded to one side of the silicon wafers, creating what we now refer to as a "preform."

We then deposited a film of CsN_3 into the preform through a shadow mask, which ensures that the film covers only the inner glass window and not the silicon surface. Commercially obtained CsN_3 powder was placed in a custom thermal evaporation chamber that was then evacuated to a base pressure of 1.3×10^{-4} Pa (1×10^{-6} Torr). The CsN_3

[a]Electronic mail: liew@boulder.nist.gov

Downloaded 09 Jan 2008 to 132.163.52.58. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

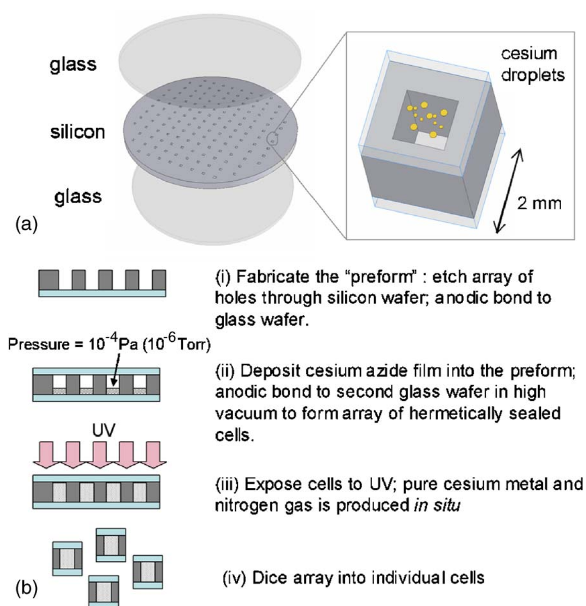

FIG. 1. (Color online) (a) Exploded schematic of a wafer of cells and schematic of a single cell after fabrication and dicing. (b) Batch fabrication and filling process.

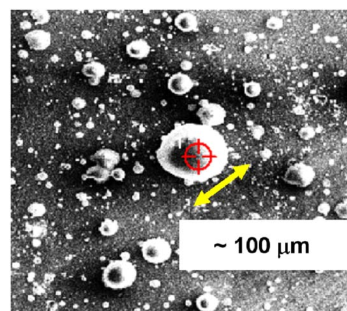

FIG. 2. (Color online) (a) Scanning electron micrograph of deposited CsN_3 film. The cross indicates where EDS measurement was done.

was heated in stages and at a rate of about 2 °C/min and held at 250 °C for several hours. The temperature was then slowly increased to the melting point of 310 °C and held there for several minutes to enable uniform melting.

As with most ionic compounds, CsN_3 tends to thermally decompose when heated. Although other researchers have found that thermal dissociation of CsN_3 is negligible in vacuum[9] and that the compound can also exist in the vapor phase,[8] nevertheless azides, in general, tend to be thermally unstable and detonate upon heating, this instability being highly sensitive to impurities. In our deposition experiments there was a tendency for the CsN_3 to self-heat, resulting in large temperature and pressure fluctuations, leading to rapid decomposition followed by explosion within the vacuum chamber. This effect is possibly due to impurities or material defects that can alter the rate and mechanism of the azide decomposition.[10] "Splattering" was also observed, accompanied by sudden fluctuations in pressure on the order of 6.7×10^{-4} Pa (5×10^{-6} Torr) and sudden increases in the deposition rate and thickness. Thus, the deposition was achieved through a combination of slow, controlled vacuum evaporation and occasional uncontrolled splattering. Techniques we have found that lessen the likelihood of these instabilities include thermal cycling, temperature soaks at various intermediate temperatures, and varying the heating/cooling rates. Once a stable temperature and pressure were reached at or slightly above the CsN_3 melting point, the deposition shutter was opened and the temperature was increased to 320–350 °C. Deposition rates varied from 0.1 to a few nm/s, with a pressure of 1.3×10^{-3} Pa (1×10^{-5} Torr). Typical thicknesses deposited were between 100 and 500 nm as measured by the quartz crystal sensor, although the occurrence of splattering makes the measured thickness somewhat inaccurate.

The deposited films are nonuniform and consist of agglomerates ranging in size from a few micrometers to a hundred micrometers in diameter (see Fig. 2). Between the agglomerates is a layer, covering the substrate, which is too thin to be imaged by scanning electron microscopy as the film would dissociate in the electron beam. Qualitative elemental analysis of the films via energy dispersive spectroscopy (EDS) indicated the presence of nitrogen in the films, as expected.

Since the mechanisms of CsN_3 dissociation are not well understood,[10] we speculate that some thermal decomposition (followed by possible recombination or formation of other compounds such as nitrides) could occur in parallel with the deposition process. The final film could thus be a mixture of cesium compounds, including but not limited to the azide. As a reference, additional cells were made in which CsN_3 powder straight from the bottle was manually placed in the preform cavities, as opposed to being evaporated. Optical spectroscopy of these cells, following vacuum sealing and photodecomposition, produced results similar to those for the cells containing the azide films, thus suggesting that the films are at least partially composed of cesium azide as well.

After azide deposition, the preform was baked at 200 °C in a custom high vacuum anodic bonding chamber for several hours. A Pyrex wafer was then anodically bonded to the silicon side of the preform while the chamber pressure was 6.7×10^{-4} Pa (1×10^{-6} Torr). The wafer stack was then irradiated under a UV lamp of 254 nm wavelength and an intensity of 0.023 mW/mm^2, over various periods ranging from 8 h to over 100 h. The cesium produced by the azide photochemical decomposition is visible under a microscope as gold-colored metallic droplets on the inner cell window (see Fig. 3). Whereas the photolysis of other metal azides such as barium azide[11] is known, the photolysis of CsN_3 has not been previously demonstrated. Finally, the wafer stack was diced into individual cells. The external dimensions of a single cesium cell may be as small as $2\times2\times1.75$ mm^3.

The photolysis of the CsN_3 film into pure cesium and nitrogen gas was confirmed by optical spectroscopy. First, the cell was heated to a temperature of 75–120 °C to increase the cesium atomic density. The wavelength of a commercial vertical cavity surface emitting laser (VCSEL) was scanned over the cesium $D2$ transition at 852 nm by modulating the injection current. Light from the VCSEL was then passed through the cell, and the characteristic cesium absorption spectrum, consisting of two peaks separated by the ground-state hyperfine splitting of ^{133}Cs (9.2 GHz), was detected by a commercial photodiode placed behind the cell (see Fig. 3). The pressure of the N_2 buffer gas may be estimated by comparing the broadening and shift of the spectral line with that from a reference cesium cell without buffer gas. Furthermore, by varying the amount of azide deposited and the UV irradiation time, various N_2 buffer gas pressures,

Downloaded 09 Jan 2008 to 132.163.52.58. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

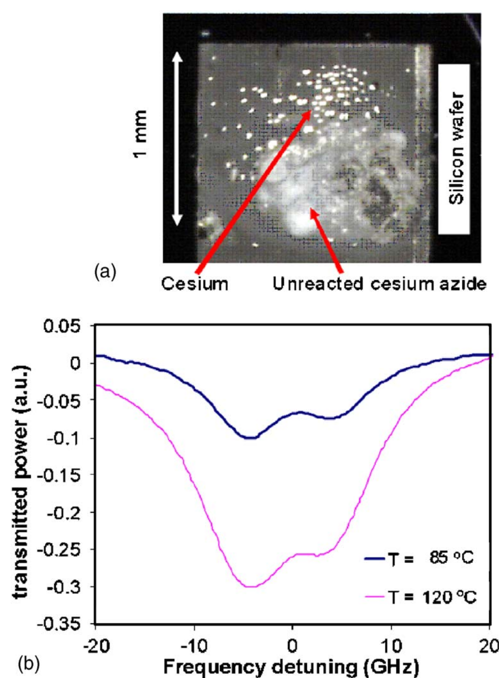

FIG. 3. (Color online) (a) Photograph of a cell, viewed through the glass window, showing the cesium produced *in situ* from azide photodecomposition. Most cells contain less azide than shown in this figure. Here a cell with more unreacted azide is shown for clarity. (b) Cesium optical absorption spectrum obtained from a cell in which a film of CsN_3 was deposited and photodissociated. The N_2 buffer gas pressure is estimated from the line broadening to be about 350 Torr at room temperature.

which in our experiments range from 27 kPa to over 270 kPa (about 200–2000 Torr), may be obtained. The cells are more optically transparent than in our previous work[4] because they contain no bulk oxides or residues except for a thin film of unreacted azide. Furthermore, cells have been made which show no noticeable change in the optical absorption linewidth or contrast after one year. This suggests that the chemical environment within the cell is stable, which is important for the functioning of atomic-based instruments.

Figure 4 shows a cesium coherent population trapping (CPT) resonance[12] obtained from a cell in which azide had been photolysized. The laser current was modulated at 4.6 GHz (close to one-half of the ground-state splitting of Cs). The first-order modulation sidebands were kept in resonance with the corresponding optical transitions starting from the two ground-state components. The microwave frequency was scanned in a 20 kHz interval, and the transmission through the cell increased when it matched exactly one-half of the atomic ground-state splitting, creating the resonance. The CPT linewidth of 2.7 kHz suggests that narrow linewidths are possible from azide-derived cesium cells.

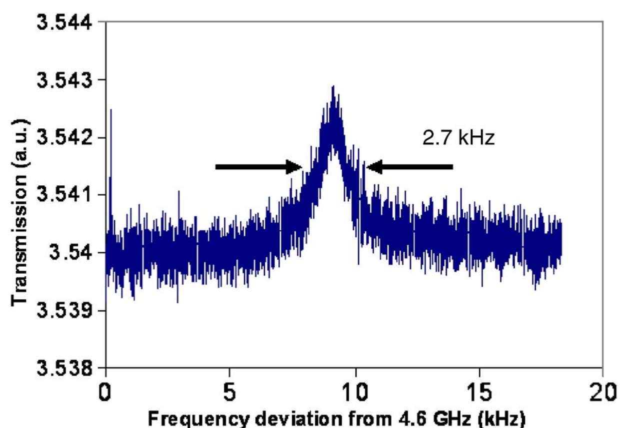

FIG. 4. (Color online) CPT transmission for a CsN_3-derived cell. The N_2 buffer gas pressure in this cell was about 37.3 kPa (280 Torr).

For clock applications, temperature compensation could be obtained by prefilling the anodic bonding chamber with other buffer gases before cell sealing. Furthermore, this technique allows for creation of high buffer gas pressure inside the cell. For magnetometer applications where only the high buffer gas pressure is desired and temperature compensation is not as critical, these N_2 buffer gas cells may be sufficient in their present form.

In summary, we have demonstrated thin-film deposition and photodecomposition of cesium azide for filling microfabricated atomic resonance cells. This method replaces the technically complex and limiting process of handling liquid cesium with a remote and wafer-level *in situ* production of the cesium. This method also combines the formally disparate functions of cell *fabrication* and cell *filling* into one seamless procedure that is readily amenable to massively parallel processing, a feature which may be critical to future commercialization of CSADs. Furthermore, these cells are devoid of noncesium chemical residues that might react over time with the cesium; thus the cells remain chemically pure and the cell windows optically clear. Finally, this technique allows for a careful control of the final buffer gas pressure through varying the film deposition and photolysis parameters.

This work was supported by the U.S. Defense Advanced Research Projects Agency's Microsystems Technology Office. The authors thank Svenja Knappe, Ying-Ju Wang, and John Kitching at NIST for valuable technical discussions, and Daniel Porpora at NIST for assistance with thermal evaporator construction. This work is a contribution of the National Institute of Standards and Technology and is not subject to U.S. copyright.

[1]S. Knappe, L. Liew, V. Shah, P. Schwindt, J. Moreland, L. Hollberg, and J. Kitching, Appl. Phys. Lett. **85**, 1460 (2004).
[2]R. Lutwak, J. Deng, W. Riley, M. Varghese, M. Mescher, D. Serkland, and G. Peake, Proceedings of the 36th Annual Precise Time and Time Interval (PTTI) Systems and Applications Meeting, Washington, D.C., 7–9 December 2004.
[3]P. D. D. Schwindt, S. Knappe, V. Shah, L. Hollberg, J. Kitching, L. Liew, and J. Moreland, Appl. Phys. Lett. **85**, 6409 (2004).
[4]L. A. Liew, S. Knappe, J. Moreland, H. Robinson, L. Hollberg, and J. Kitching, Appl. Phys. Lett. **84**, 2694 (2004).
[5]S. Knappe, V. Gerginov, P. Schwindt, V. Shah, L. Hollberg, and J. Kitching, Opt. Lett. **30**, 2351 (2005).
[6]C.-H. Lee, H. Guo, S. Radhakrishnan, and A. Lal, Proceedings ot the Solid-State Sensor, Actuator and Microsystems Workshop (Hilton Head 2004), Hilton Head Island, SC, 6–10 June 2004, pp. 23–26.
[7]S. Radhakrishnan and A. Lal, Proceedings of the 13th International Conference on Solid-State Sensors, Actuators and Microsystems (Transducers 2005), Seoul, Korea, 5–9 June 2005, pp. 23–26.
[8]J. S. Ogden, J. M. Dyke, W. Levason, F. Ferrante, and L. Gagliardi, Chem.-Eur. J. **12**, 3580 (2006).
[9]Y. Sears and M. Steinberg, Thermochim. Acta **75**, 233 (1984).
[10]B. L. Evans, A. D. Yoffe, and P. Gray, Chem. Rev. (Washington, D.C.) **59**, 515 (1959).
[11]E. G. Prout, E. G. Shephard, and C. T. O'Connor, J. Inorg. Nucl. Chem. **43**, 643 (1981).
[12]E. Arimondo, in *Progress In Optics*, edited by E. Wolf (Elsevier, Amsterdam, 1996), Vol. 35, pp. 257–354.

Downloaded 09 Jan 2008 to 132.163.52.58. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp