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Gallium phosphide as a new material for anodically bonded atomic sensors

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Miniaturized atomic sensors are often fabricated using anodic bonding of silicon and borosilicate glass. Here we describe a technique for fabricating anodically bonded alkali-metal cells using GaP and Pyrex. GaP is a non-birefringent semiconductor that is transparent at alkali-metal resonance wavelengths, allowing new sensor geometries. GaP also has a higher thermal conductivity and lower He permeability than borosilicate glass and can be anodically bonded below 200 °C, which can also be advantageous in other vacuum sealing applications. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4891375>]

Anodically bonded cells containing alkali-metal atoms have recently found several applications in atomic sensor technology. They are used in miniature atomic clocks,¹ magnetometers,² and nuclear spin gyroscopes.³ These applications typically use anodic bonding of silicon and a borosilicate glass, such as Pyrex or Borofloat.⁴ Anodic bonding allows chemical-free vacuum sealing of cells which is compatible with alkali-metal atoms and batch-fabrication technology. Borosilicate glass is relatively resistant to reaction with alkali metals and has an excellent match of the coefficient of thermal expansion with silicon.

However, silicon-borosilicate glass anodically bonded cells have certain limitations in experimental geometries because silicon is not transparent to near-infrared light that is used for optical pumping and probing of alkali-metal atoms. For example, pump-probe geometries typically use a cell oriented at 45° in order to obtain optical access for two orthogonal laser beams.⁵ Borosilicate glass also has limitations in having relatively high permeability to He gas, which has an effect on atomic clock frequency stability.⁶ Low thermal conductivity of glass also limits the thermal time constant and temperature uniformity in the cell.

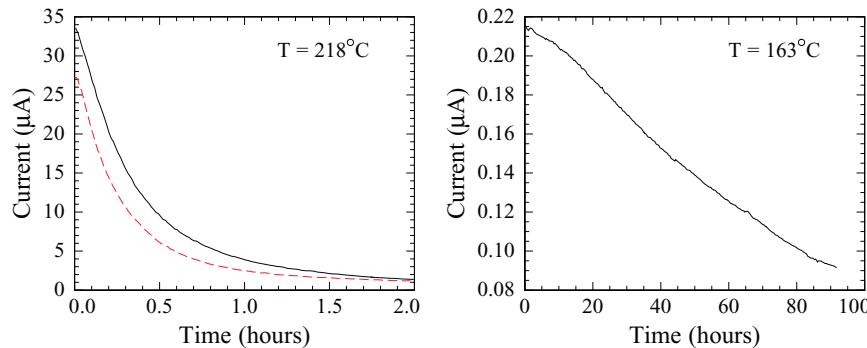
In this letter, we describe an alternative material that can be used in anodically bonded alkali-metal cells. The main requirements are that the material is transparent in the near infrared and is not birefringent. We find that GaP fits these requirements. GaP has a band gap of 2.2 eV, so it is transparent for wavelengths above 550 nm. GaP has a cubic lattice and therefore has only a very small spatial-dispersion induced birefringence.⁷ Its coefficient of thermal expansion is slightly larger than Pyrex and silicon, but we find that it can be reliably anodically bonded to Pyrex. We are not aware of previous reports of GaP anodic bonding in the literature; anodic bonding of GaAs to Corning 0211 glass has been previously described in Ref. 8. We have fabricated cells using GaP and Pyrex or Borofloat glass in several geometries. Some of the physical properties of GaP are shown in Table I for reference.

GaP has a high refractive index at the near infrared wavelength, $n_{\text{GaP}} = 3.2$. As a result, uncoated GaP has large reflection losses. We find that a single quarter-wave layer of Al₂O₃ can be used quite effectively as an anti-reflection coating, since the index of refraction of Al₂O₃ is close to satisfying the relationship $n_{\text{Al}_2\text{O}_3} = \sqrt{n_{\text{GaP}}}$. Al₂O₃ also improves the chemical stability of GaP when exposed to Rb vapor at high temperature. Without Al₂O₃ coating GaP is stable against Rb at 150 °C, but

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TABLE I. Relevant physical properties of GaP.

Properties of GaP at room temperature	
Band gap	550 nm
Index of refraction at 795 nm	3.2
Thermal expansion coefficient	$4.8 \times 10^{-6} \text{ K}^{-1}$
Thermal conductivity	110 W/mK

FIG. 1. Current during anodic bonding of GaP (black lines) and silicon (red dashed line) to Pyrex. The bonding area is about 1 cm^2 and applied voltage is 1.5 kV.

turns black above 200°C after several days. With Al_2O_3 coating we have not seen a degradation of the transmission through a Rb cell with GaP windows heated for a month to 210°C .

Helium gas permeation is a significant problem in borosilicate glass cells. Possible issues include both leaking of He buffer gas out of the cells and leaking of He from the atmosphere into the cells which degrades the vacuum and causes long-term frequency drifts in atomic clocks. We expect GaP to have a very small permeability to He, as is the case for other single crystal semiconductors.⁹ We have measured the permeation of He through GaP and found it to be at least 100 times smaller than for Pyrex.

Anodic bonding of GaP to Pyrex proceeds in steps similar to silicon-Pyrex bonding. We used undoped single-crystal GaP 0.5 mm thick wafers in [111] orientation. This crystal orientation eliminates already small effects of spatial-dispersion induced birefringence present in all cubic crystals.⁷ We used commercial Pyrex windows and Borofloat wafers as well as glass-blown Pyrex cells with open ends whose edges were polished to $\lambda/2$ flatness and 5-10 scratch-dig quality. The surfaces were cleaned in Piranha solution and rinsed in de-ionized water. The pieces to be bonded are set on a hot plate in air under light pressure of about 10 kPa. We used the highest possible voltage during bonding to maximize ion flow at low temperature. The voltage was increased until just below onset of sparking and typically reached 1.5 kV. When attaching GaP at the ends of cylindrical glass cells, the electrical contact to the glass surface was made using a wire braid wrapped around the body of the cylinder as close as possible to the bonding surface to minimize the current path in the glass. The glass cells typically had 1.5-2 mm wall thickness to ensure adequate edge area for vacuum-tight sealing. Anodic bonding was performed at a few different temperatures, examples of the current flow during bonding at 218°C and at 163°C are shown in Figure 1. The current flow for GaP-Pyrex bonding is similar to silicon-Pyrex bonding. The total charge transferred during bonding was independent of temperature and equal to $40\text{--}80 \text{ mC/cm}^2$, near the upper range of charge transfers observed in glass anodic bonding.^{10,11} Vacuum-tight bonding could be accomplished at temperatures as low as 150°C after several days of bonding time, significantly lower than the temperature typically used for anodic bonding.¹² Lower bonding temperature is preferred for GaP bonding to borosilicate glass in order to reduce stresses due to mismatch of the thermal expansion coefficients. We found that quarter-wave Al_2O_3 coating on GaP does not impede anodic bonding, the bonding can proceed

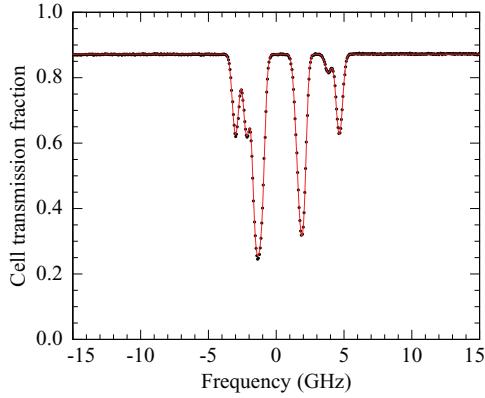


FIG. 2. Absolute transmission through a Rb vapor cell with two GaP windows coated on both sides with Al_2O_3 single layer anti-reflection coating. The cell is heated to 62°C and the transmission is fit to a Doppler-broadened Rb absorption spectrum.

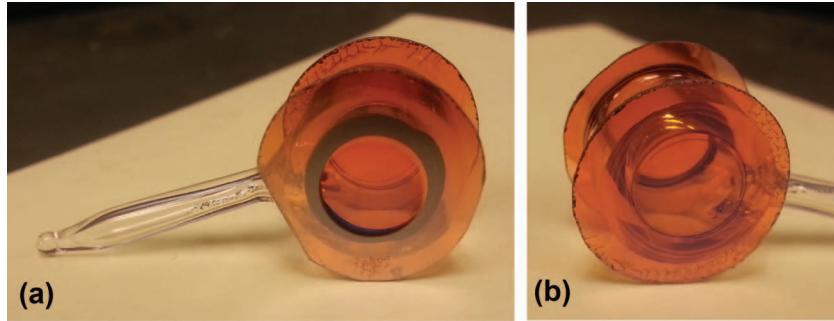


FIG. 3. Anodically bonded GaP-Pyrex Rb vapor cell. Panel (a) shows GaP window with a central Al_2O_3 coating, and panel (b) shows the window with the coating covering all surface, including the anodic bonding region. Opacification of GaP due to exposure to high temperature Rb vapor can be seen in the uncoated region in panel (a).

through the coating. In addition to cylindrical glass cells sealed with GaP end windows, we also bonded GaP and Borofloat wafers and made sandwiches of GaP - 0.2 mm Pyrex - GaP.

GaP wafers coated with a single quarter-wave layer of Al_2O_3 coating on both sides had a total reflection of 2% and transmission of 96.5% at 795 nm. Thus, the absorption losses in the 0.5 mm thick wafer were 1.5%, probably limited by material impurities. In Fig. 2, we show the absolute transmission of the light near Rb D1 line through a Rb-filled cell without buffer gas. Outside of resonance region, the transmission through two GaP windows coated with Al_2O_3 is equal to 87%. We believe additional losses are due to thin coating of Rb on the cell windows, something that is commonly observed with glass windows as well. The transmission through the cell did not show any degradation after exposure to Rb vapor at high temperature. Figure 3 shows a picture of one of the cells filled with Rb. Two sides of the same cell are shown. One GaP window had only a central circular region coated with Al_2O_3 , avoiding the anodic bonding area. After exposure to Rb vapor at 200°C for several days, one can see an annular dark region, where the bare GaP reacted with Rb. The second GaP window was completely coated with Al_2O_3 and anodically bonded through the coating.

We studied helium permeability through GaP by anodically bonding two glass tubes with 14 mm inner diameter on opposite sides of an uncoated GaP wafer. One tube was connected to a vacuum system with a quadrupole mass spectrometer, the other tube was connected to a reservoir filled with helium gas. The wafer was heated to 200°C for several days to allow He to diffuse into the 0.5 mm thick GaP and establish an equilibrium flow. The helium flow rate was measured by closing the vacuum pump and measuring the rate of helium concentration raise with the mass spectrometer. To check the procedure we also measured the permeation of helium through a 0.5 mm thick Pyrex wafer in similar geometry. For Pyrex, we find the permeability constant $k = 4.2 \times 10^{-9} \text{ cm}^2/\text{s}$, close

to previously measured values at 200 °C.¹³ For GaP, we find $k = (4 \pm 4) \times 10^{-11}$ cm²/s. It is likely the permeation rate is lower, but we were limited by background helium leakage in our system.

In conclusion, we have investigated GaP as a promising material for construction of anodically bonded cells for atomic sensors. Optical transparency in the near infrared, low birefringence, low permeability to helium, and high thermal conductivity make it an attractive choice in these applications. The high index of refraction of GaP requires application of an anti-reflection coating, a single layer of Al₂O₃ is sufficient for this purpose and also serves to increase the chemical resistance of GaP to alkali-metal vapor. Using voltages greater than 1 kV, we were able to achieve vacuum-tight anodic bonding after several days at temperatures of 150–160 °C. Such low-temperature slow anodic bonding at high voltage may also be useful for making cells with anti-relaxation surface coatings¹⁴ and other temperature-sensitive components. The high refractive index of GaP can also enable new geometries by using it as a lens for efficient light collection.¹⁵ The electro-optic properties of GaP¹⁶ can also be used to create an integrated polarization modulator without the birefringence associated with common electro-optic materials such as LiNbO₃. Low permeability to helium may also make GaP an attractive material for transparent windows in vacuum systems used for laser-cooled atoms¹⁷ and for other purposes.

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