Copper Doped GaAs Infrared Filter for the 8-13 μm Atmospheric Window

F. R. Ruhge and R. E. Peale
Department of Physics, University of Central Florida, Orlando, FL 32816-2385

ABSTRACT

High temperature diffusion of Cu into GaAs was used to prepare infrared filters for the 8 – 13 μm atmospheric transmission window. Copper was evaporated to thickness ~ 100 nm on both sides of double-side polished 1.7 mm thick GaAs samples, then sealed in evacuated quartz ampoules back filled with 250 torr of helium. The ampoules were heated at temperatures between 600 C and 1200 C for periods of 15 min to 16 hours, and then quenched in water. Infrared spectra were collected using a Fourier spectrometer at 1.7 K – 20 K sample temperature, 500 to 3500 cm^{-1} spectral range, and 1 cm^{-1} resolution. The well known Cu:GaAs sharp-line absorption spectrum was observed near 1200 cm^{-1} together with a strong photo-ionization band at higher wave numbers. The latter provides zero transmission for wavelengths shorter than 8 μm. The sharp cut-off shifts to longer wavelengths as diffusion times and temperature increase. This process allows for the simple preparation of infrared long pass filters. The concentration profile was modeled to better understand the relation between Cu concentration and spectrum.

Keywords: GaAs, Copper, infrared, filter

1. INTRODUCTION

Infrared filters are necessary to match the spectral band pass of optical or spectroscopic systems to wavelength regions of interest, such as atmospheric transmission windows. Filters exclude solar or thermal photons with wavelengths outside the interest region. This reduces photon noise and allows for gain increase at the detection system. An important infrared wavelength region is the 8 – 13 μm atmospheric transmission window.[1] Two common types of filters are available for this range: band pass filters based on interference within surface films on a transparent substrate and long-pass filters based on scattering from diamond particles at cryogenic temperatures on polyethylene. [2, 3, 4] Both types of filters are susceptible to surface damage, which results in near-infrared leaks. There are no suitable bulk absorption filters available commercially for the 8 – 13 μm window.

An advantage of absorption filters is that surface damage does not cause out-of-band leakage. Long-pass filters based on bulk absorption are common at visible and near infrared wavelengths, for example the well-known colored-glass filters from Schott. Infrared long-pass filters can be based on fundamental absorption in semiconductor crystals, but the choice of material with suitably small band gap is very limited. Only alloys of HgTe (Eg = -0.3 eV) and CdTe (Eg = 1.6 eV) can provide a variable set of cut-off wavelengths in the 8 – 13 μm (Eg = 0.15 – 0.09 eV) range. HgCdTe is typically melt grown in a high temperature furnace. All three elements in this alloy are toxic. Stability of the cut-off wavelength is an issue because of the volatility of Hg. While this material is well known for detectors out to about 20 μm, it is unknown as a commercial filter.

This paper reports an innovative, low cost means for producing filters for the 8 – 13 μm window. These filters are based on electronic absorption by copper acceptor impurities dispersed by diffusion in single crystal GaAs. GaAs double-side polished wafers are commercially available from many suppliers at low cost. By evaporating Cu on the GaAs surface and annealing in a controlled ambient, Cu impurities diffuse into the bulk and bind holes at low temperature. The photo ionization of these bound holes to the valence band provides the bulk absorption on which the filter is based. The energy threshold for photo-ionization provides an infrared short-wavelength cut-off for the filter in the range 8-12 μm. GaAs bulk phonon absorption begins at ~17 μm, so that the proposed filters span the 8-13 μm range with a selectable short-wave cut-off.

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Absorption-type filters have potential thermal problems in high flux applications since the absorbed out-of-band radiation is converted to heat. This can cause thermal strain and fracture. However, GaAs (like many crystalline semiconductors) has very high thermal conductivity, 3 W/cm-K at 4K.[5] Hence, GaAs filters are unlikely to suffer the consequences of localized optical heating, and the generated heat may be removed easily by conduction.

2. THEORETICAL CONSIDERATIONS

Spectral results were compared with calculated Cu diffusion profile to ascertain the relation between Cu concentration and cut-off wave length. Eqn. 1 gives the Cu concentration at some depth x within the GaAs at some diffusion time t for diffusion from both surfaces of the sample.[6]

$$N(x,t) = N_0(T)\left(1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{2n+1}\sin\left(\frac{(2n+1)\pi x}{L}\right)e^{\left(-\frac{t(2n+1)^2\pi^2 D}{L^2}\right)}\right) \quad (1)$$

The thickness of the sample is L, and D is the diffusion constant. In this model $N_0(T)$ is the saturation concentration (solubility) of the Cu in GaAs with dependence on temperature T given by Eqn. 2.[7] Figure 1 displays the dependence of solubility on temperature as described by Eqn. 2.

$$N_0(T) = 3.7x10^{23}\ \mathrm{cm}^{-3}\, e^{\frac{-1.3\,\mathrm{eV}}{kT}} \quad (2)$$

The temperature dependence of the diffusion constant D for Cu in GaAs is given in Eqn. 3 [8].

$$D(T) = c_1 e^{\frac{-c_2}{kT}} \quad (3)$$

Reference 8 gives values for the coefficients, $c_1 = 3\times10^{-2}\ \mathrm{cm}^2/\mathrm{s}$ and $c_2 = 0.53\,\mathrm{eV}$. Eqn 3 is plotted in Figure 2 for the extended temperature range 100 C to 1200 C. Figure 3 shows the rapid progression to saturation expected with increasing diffusion time in the sample at the lowest diffusion temp studied of 600 C. Saturation is even more rapid at higher temperatures.

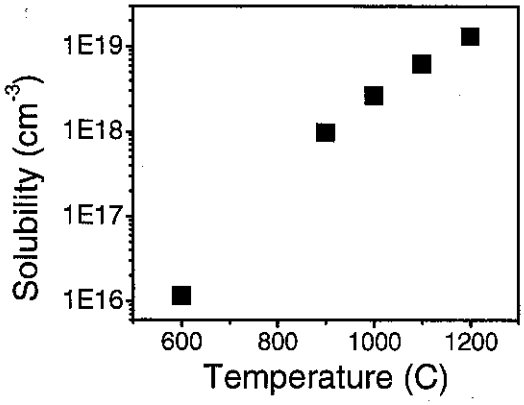

Figure 1: A plot of the solubility at each of the diffusion temps used to prepare samples, from Eqn. 2.

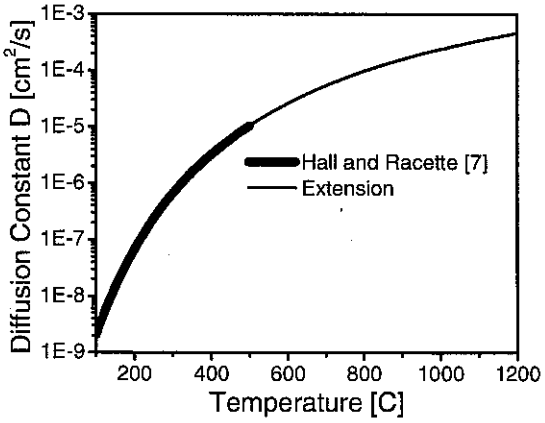

Figure 2: Temperature dependence of the diffusion constant for Cu in GaAs.

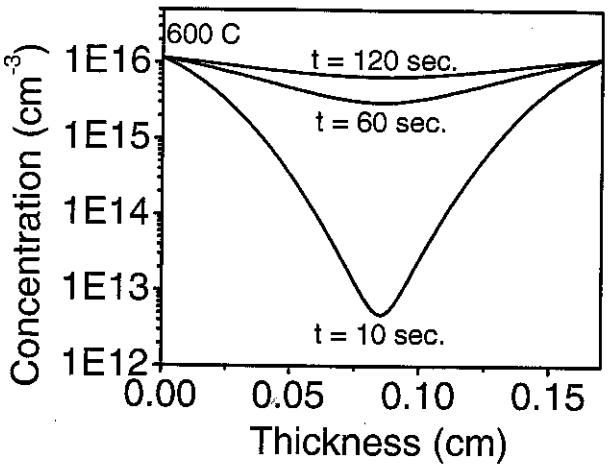

Figure 3: The theoretical concentration profiles, diffusion temperature and times are indicated on the plot.

2. EXPERIMENTAL DETAILS

Double side polished, semi-insulating GaAs was purchased from Sumitomo. These wafers were 1.7 mm thick and were cut into 5 x 10 mm rectangular samples. Copper was evaporated on each polished surface to a thickness of ~100 nm. Each piece was placed at the sealed end of a quartz tube, which was evacuated, then back filled with a 250 torr of helium, and finally sealed using a torch. Each sealed ampoule was heated in a combustion-tube furnace for different times (0.25 – 16hr) and at different temperatures (600 – 1200 C), then quenched in water. The samples were then removed from the ampoules for testing. Transmission spectra were collected at 1 cm^{-1} resolution and 1.7 K sample temperature using a Fourier transform spectrometer and an optical-access liquid-helium cryostat.

3. EXPERIMENTAL RESULTS

Fig. 4 displays transmission spectra of samples prepared by 15 min diffusion at selected temperatures. Increased diffusion temperature moves the cut-off wave number to lower values. The cut-off wave number for the samples processed at 1000 C, 1100 C, and 1200 C are 1360 cm^{-1}, 1160 cm^{-1}, and 1120 cm^{-1} respectively. These wavenumbers are determined at the point when transmission is 10% of the maximum. The sample processed at 1000 C shows the presence of three Cu absorption lines at approximately 1200 cm^{-1}. These three lines are associated with the 0.15 eV acceptor level of Cu in GaAs.[9] At diffusion temperature 1100 C these absorption lines have disappeared and a new line appears at approximately 970 cm^{-1}. This line itself disappears when the diffusion temperature is increased to 1200 C.

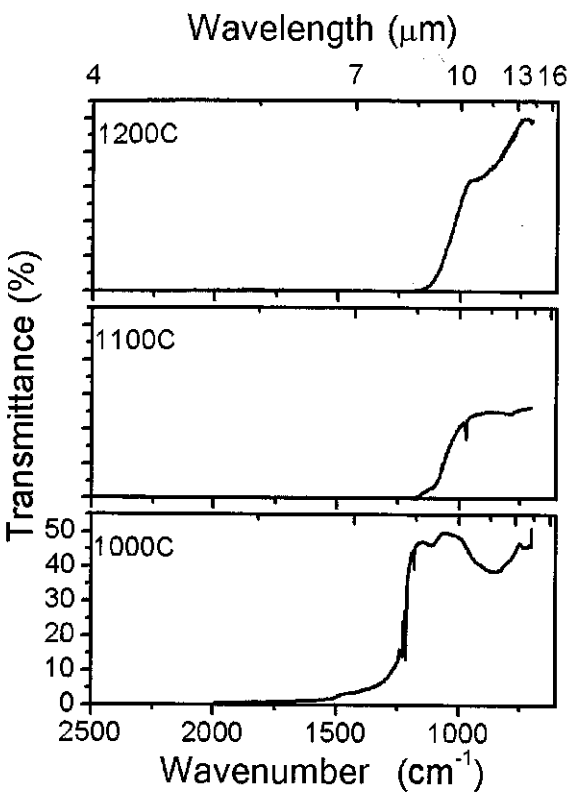

Figure 4: Transmission spectra of samples prepared by 15 min diffusion at selected temperatures.

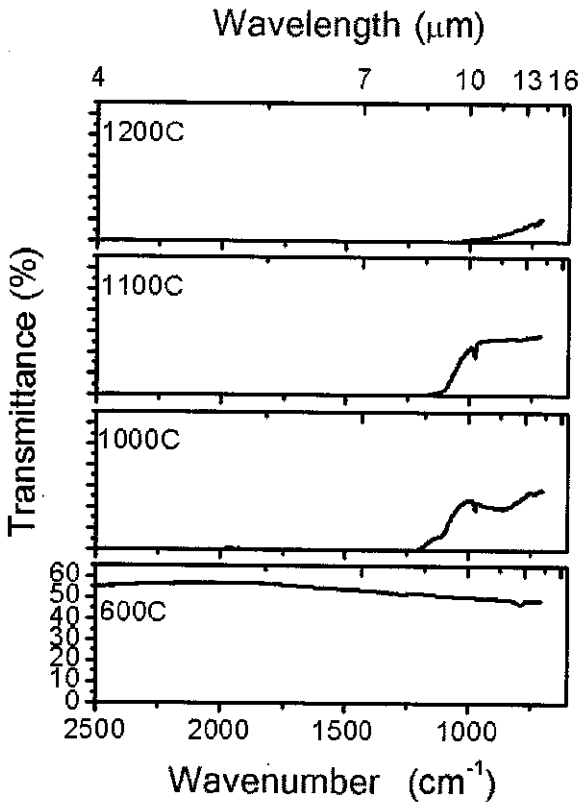

Figure 5: Transmission spectra of samples prepared by one-hour diffusion at selected temperatures.

Figure 5 displays transmission spectra of samples prepared by one-hour diffusion at selected temperatures. Increasing diffusion temperature again causes the cut-off wavelength to increase. The cut-off wavenumbers for the samples processed at 1000 C and 1100 C and are 1170 cm^{-1} and 1090 cm^{-1} respectively. Diffusion at 600 C for one hour is not sufficient to produce short wave absorption while diffusion at 1200 C pushes the cut-off wavenumber to about 700 cm^{-1}.

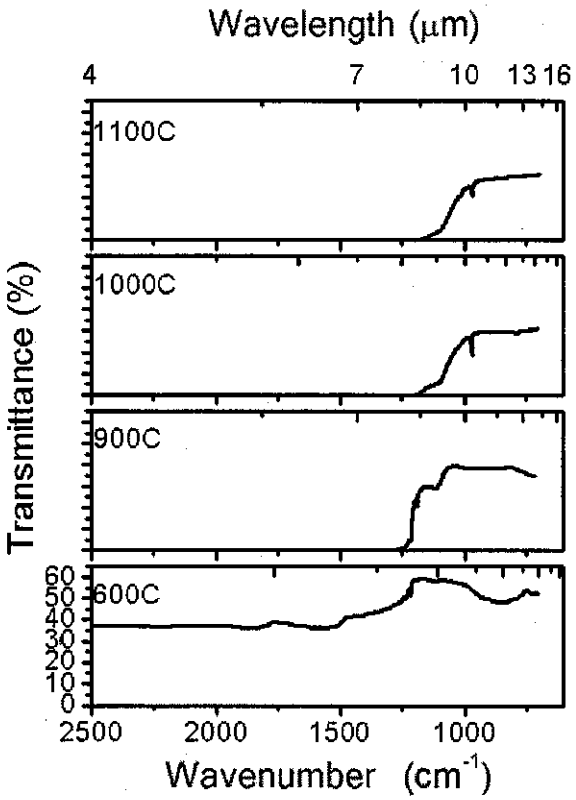

Figure 6: Transmission spectra of samples prepared by four-hour diffusion at selected temperatures.

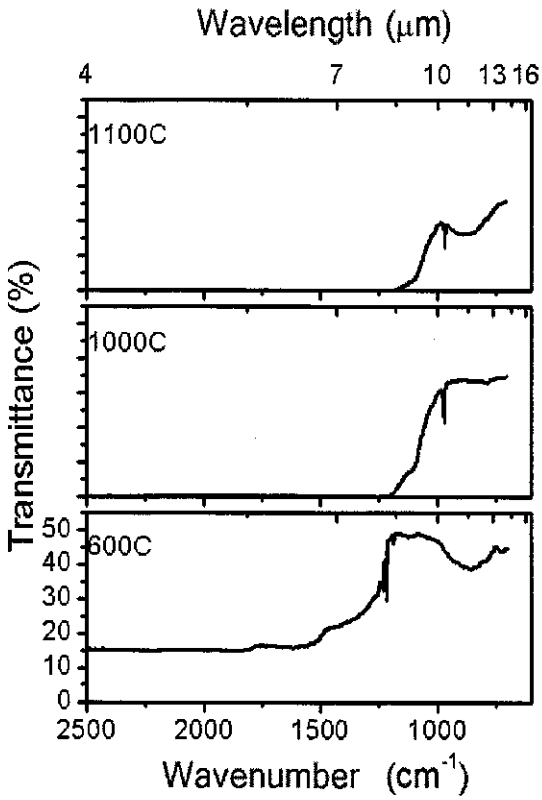

Figure 7: Transmission spectra of samples prepared by 16-hour diffusion at selected temperatures.

Figure 6 displays transmission spectra of samples prepared by four-hour diffusion at selected temperatures. As temperature increases the cut-off wave length shifts to longer values. For 600 C diffusion temperature, some copper-absorption begins to be apparent at this diffusion time, but out of band transmission is still high. At 900 C, 1000 C, and 1100 C, the cut off wavenumbers are 1220 cm^{-1}, 1160 cm^{-1}, 1120 cm^{-1}, respectively. The Cu absorption lines are slightly present in the 900 C sample and absent in the 1000 C and 1100 C samples, where the 970 cm^{-1} line appears.

Figure 7 displays transmission spectra of samples prepared by 16-hour diffusion at selected temperatures. At 600 C, the copper-absorption is strong, but out-of-band transmission is still high. The Cu absorption lines while the 970 cm^{-1} line appears in the 1000 C and 1100 C samples. The cut-off wavenumbers for the 600 C, 1000 C, and 1100 C samples are 1500 cm^{-1}, 1160 cm^{-1}, and 1120 cm^{-1}, respectively.

Figure 8 displays the temperature dependence of a sample spectrum. The sample used was prepared by 1000 C diffusion for 15 minutes. Absence of sharp Cu absorption lines at 20 K indicates substantial thermal ionization of the copper acceptors, which is accompanied by a small increase in out-of-band transmission.

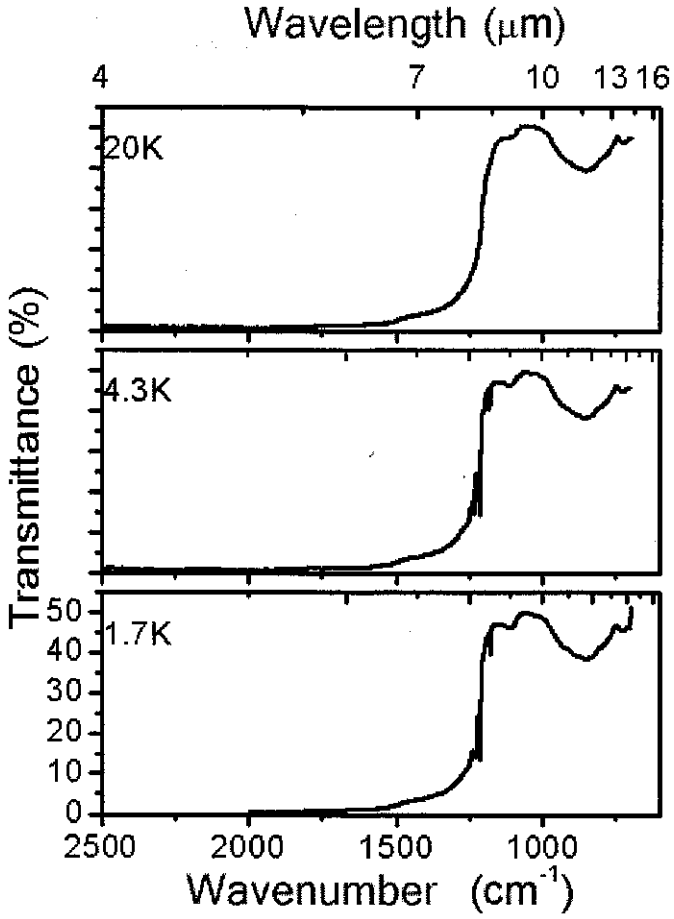

Figure 8: Temperature dependence of Cu:GaAs prepared by 15 min 1000 C diffusion.

4. DISCUSSION

The simulation of copper diffusion profiles suggests that all of the samples prepared should be uniformly doped with Cu at the saturation limit $N_0(T)$. Fig. 3 indicates that even for temperatures as low as 600 C the sample should be fully saturated with Cu in just two minutes. However, the data presented here shows that Cu-related absorption is not observed at all until the sample has been heated for about 4 hours at 600 C. Moreover the absorption strength continues to grow for diffusion times up to 16 hours. This suggests that the effective value of the diffusion constant for forming isolated Cu acceptors at 600 C is much smaller than the value reported by Hall and Racette[8] and used to produce Fig. 3. The purpose of the rapid quench after sample processing was to freeze in the concentration of isolated Cu acceptors at the saturation level corresponding to the diffusion temperature T. However, the samples continue to glow for a few seconds within their sealed ampoules, so it can be expected that some relaxation of isolated Cu concentration might occur in favor of complex formation.

Due to the high refractive index of GaAs (3.6), the transmittance after reflection is only~50%. Transmittance below 50% is found in some samples after diffusion and may be attributed to residual surface Cu layer or surface decomposition (samples were not re-polished after diffusion). Evidence for the later is the brown coating observed on the inside of the ampoules after heat treatment, though the polished GaAs surface remains shiny. Re-polishing the

samples after diffusion might restore transmittance near 50%, but would also partly remove material with the highest Cu concentration if the sample is not already fully saturated.

In-band transmittance might be improved by suitable anti-reflection coating using low index films. Polycrystalline films may have strong absorption in the 8 – 13 μm range particularly from ester and C-O molecular groups, although polyethylene has good transmittance in the 8 – 13 μm range.[6] Films of chalcogenides such as zinc sulfide or cadmium sulfide, which have indices near 2.0, might be deposited by low cost chemical bath methods.

The disappearance of the familiar Cu absorption lines and the appearance of the 970 cm^{-1} line indicates copper complex formation that needs to be studied further. The temperature dependence of the spectrum (Fig. 7) indicates that best filter performance will be achieved if the material is cryogenically cooled. Since detectors for this wavelength range are themselves usually cooled, cooling the filter should not introduce a significant increase in system complexity.

5. CONCLUSION

Far infrared filters for the 8 – 13 μm atmospheric transmission window were prepared by diffusion of Cu into GaAs. The cut-off wavelength is a selectable function of processing conditions. The resulting absorption-based filters are simple, rugged, and low cost compared with commercially available filters based on interference in surface films. Potential applications include astronomical imaging, spectroscopy, remote sensing, and laser free-space communications. The proposed filters are innovative for this wavelength region because they work by bulk absorption, rather than interference or scattering at surface coatings. Hence, they will be less susceptible to light leaks caused by surface damage than currently available far-IR filters for the same range.

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