Effects of wafer thermostability and wafer-holding materials on optical loss in GaAs annealing

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A periodic structure of bonded GaAs wafers has been proposed for quasi-phase-matched second-harmonic generation. However, current bonding processes used to fabricate these structures often lead to unacceptably high optical losses. When commercial semi-insulating GaAs wafers were bonded at 850 °C, increases in the free-hole concentration (thermal conversion) were found to be a major cause of excess optical loss. This conversion depended on both the GaAs source and the materials comprising the sample holder. We found that quartz and sapphire could not be used in contact with GaAs wafers because they stuck during the bonding process. On the other hand, As-charged graphite holders did not stick and worked well under our bonding conditions. © *1998 American Institute of Physics.* [S0021-8979(98)06210-0]

Bonding of III–V semiconductors was originally developed for two-layer optoelectronic devices.[1,2] Based on these studies, a periodic structure of bonded GaAs wafers has been proposed for quasi-phase-matched (QPM) second-harmonic generation (SHG).[3] In a previous study,[4] we identified three kinds of defects that cause excess optical losses in these structures: (1) interfacial defects, (2) bulk defects, and (3) surface defects. An increase in bonding temperature and/or time led to a decrease in interfacial defects, but an increase in the bulk and surface defects. Bonding at 850 °C appeared to be a reasonable compromise.[4] At 850 °C, increases in the hole concentration (thermal conversion) were found to be the major source of excess optical loss. Thermal conversion from semi-insulating to p-type GaAs was found to depend on two factors: (1) the material(s) comprising the sample holder, and (2) the source (manufacturer) of the GaAs wafers. The emphasis in this study was to determine the relationship between the optical losses in individual thermally processed GaAs wafers, the holder materials (graphite, quartz, and/or sapphire) in contact with the GaAs wafers during the bonding process, and the source of the wafers.

Three materials have been considered for holding GaAs wafer stacks; sapphire, quartz, and graphite. In these studies, virgin GaAs wafers were ''sandwiched'' between flat plates of various ''holder materials'' under pressure and subjected to an annealing process similar to that used for bonding multiwafer structures. The smooth surfaces of sapphire and quartz were cleaned with deionized (DI) water and isopropanol. The rough surfaces of the graphite holders were polished with No. 600 sandpaper and 1.0 μm diamond paste, and then cleaned with DI water and isopropanol. Finally, they were all baked out at 850 °C for 20 h under a flowing gas mixture of H_2(60 cc/min) and N_2(1000 cc/min).

Since both p-type and n-type conductivity cause free-carrier absorption in GaAs,[5,6] only semi-insulating wafers were used. Table I lists their specifications. The wafers were purchased from two different companies, designated as ''A'' and ''X.'' Wafers from company A, grown by the liquid-encapsulated Czochralski method, had dislocation densities $\sim 10^5$ cm^{-2}, while the wafers from company X were grown by the Bridgman method and had significantly lower densities, $\sim 10^3$ cm^{-2}. Wafers designated as ''X(100)Cr'' were Cr doped; the others were undoped. Wafers designated as ''A(110)S'' had resistivities $\sim 10^8$ Ω cm and were guaranteed by the vendor to be stable after annealing at 850 °C for 5 h in either an arsenic overpressure or under a plasma-enhanced chemical-vapor deposition (PECVD) Si_3N_4 cap. Wafers designated as ''A(110)'' were not guaranteed to be stable. All wafers were diced into 9×9 mm^2 square samples and solvent cleaned in a class-100 clean room prior to use. Single GaAs samples were then processed under the bonding conditions described in Ref. 4. [With a compressive load of 10 kg/cm^2, they were heated to 850 °C for 2 h under a flowing gas mixture of H_2(60 cc/min) and N_2(1000 cc/min).]

Even though sapphire and quartz were found to protect GaAs from thermal conversion, they usually stuck strongly to the GaAs samples, and there was no way to remove them without breaking the samples. Graphite holders, on the other hand, did not stick during annealing. When a new graphite holder was used, the optical transmission of the GaAs wafers was found to be low. These results are similar to the findings of Liau[7] during his InP thermal annealing studies in which he found that a graphite cover was inadequate protection because In vapor was able to permeate the graphite. We found that if the holders had been used previously (aged), however, higher transmittances were observed. Regardless of the manufacturer, the sheet resistance and the transmittances at 5.3 and 10.6 μm (the two critical wavelengths for doubling the CO_2 laser) improved with each successive use of the graphite holder, until a maximum was reached, as shown in

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TABLE I. Manufacturer's specifications for some semi-insulating GaAs wafers.

	A(110)	A(110)S	X(110)	X(100)Cr
Dopant	Undoped		Undoped	Cr
Resistivity	$>1\times10^7$ Ω cm[a]		$>1\times10^7$ Ω cm	
Etch pit density	$-10^5/\text{cm}^2$		$\leqslant5\times10^3/\text{cm}^2$	

[a]The resistivities of wafers A(110)S were guaranteed by the vender to be stable after annealing at 850 °C either in an arsenic overpressure or under a PECVD Si_3N_4 cap for 5 h.

Fig. 1. At this point, the optical transparency of an annealed GaAs wafer was found to be nearly the same as an unprocessed wafer. Wafer set A(110) stopped degrading after the graphite holder had been used three times. Wafer sets A(110)S, X(110), and X(100)Cr required only one prior use. Surprisingly, wafers in the second group were from different companies and had different crystallographic orientations, dopants, and dislocation densities. In other words, in our GaAs bonding process, the dislocation density (10^3-10^5 cm^{-2}), wafer orientation, and Cr dopant had little effect on the final optical loss.

Wafers in set A(110), although possessing extrinsic properties similar to wafer set A(110)S, were far less thermally stable. According to the vendor, the growth and post-growth processing procedures for A(110) and A(110)S were all the same. Discussion with the vendor reveals the only difference between these wafers was the source of the raw materials. After the vender changed to a high-purity source, the GaAs wafers were all as stable as A(110)S. These results are similar to the conclusions drawn by Ohkubo *et al.*[8,9] during their semi-insulating GaAs annealing studies. With different native acceptor (carbon) concentrations, they found that the carbon impurity enhanced the p-type conversion. Wafers from lot A(110) were definitely less suitable for fabricating periodic GaAs optical device structures. However, they were quite sensitive to whether or not the graphite holders had been used previously and were, therefore, ideal for elucidating the ''aging'' phenomenon observed.

The optical degradation observed in GaAs heat treated with ''new'' graphite holders might have resulted from two

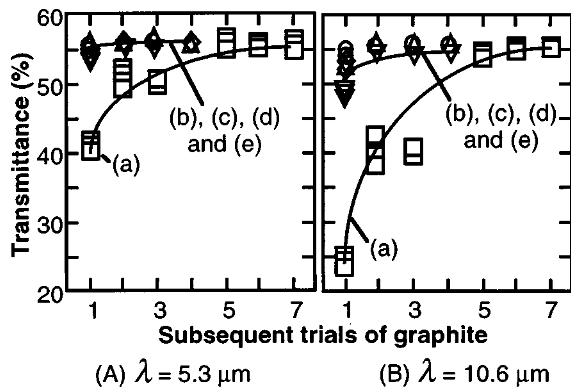

FIG. 1. Observed transmittance of the 850 °C annealed GaAs wafers: (a) A(110), (b) A(110)S, (c) X(110), and (d) X(110)Cr, with subsequent use of the graphite holder, and (e) A(110) with pyrolytic-carbon-coated graphite at different positions of the sample (edge or center).

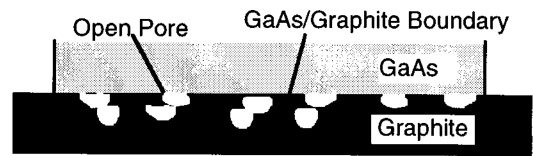

FIG. 2. GaAs/graphite interface: open pores surrounded by GaAs/graphite hermetically sealed boundaries.

mechanisms: (1) the in-diffusion of impurities into the GaAs wafers, and/or (2) the out-diffusion of As from the GaAs. Since the diffusion constant of carbon is exceedingly small,[10] the graphite holders were expected to have little effect on optical properties. With respect to impurities in the graphite holders, they would have to diffuse out of the graphite holder and into the GaAs with each successive use, thereby purifying the graphite. To test this model an ''aged'' graphite holder was heated alone to both 500 and 850 °C for 2 h in a gas mixture of H_2 and N_2. Since no other impurities could have been introduced during this reheating process, the graphite holder should have remained pure. However, when these graphite holders were again used to anneal GaAs wafers, the transmittance of the annealed wafers was found to be low, more or less in the same range as that produced by the new (unused) graphite holders. This experiment clearly eliminated the possibility of in-diffusion of impurities into the GaAs. At the same time it suggested that out-diffusion of As from GaAs was more likely to be responsible for the excess optical losses observed since loss of As from a wafer surface is known to convert the surface from semi-insulating to p type.[11]

It has been well established in the GaAs processing industry that at 850 °C, a 60 Torr As overpressure is needed to prevent As loss from free GaAs surfaces.[12] We, therefore, considered a simple model that would allow an As-charged graphite holder to maintain a 60 Torr As overpressure in the vicinity of the GaAs surface. Scanning electron microscope analysis of the graphite holder surfaces indicated the presence of numerous pores with an average opening on the order of 1–10 μm. During annealing, the GaAs wafer/graphite holder interfaces are held firmly together under a 10 kg/cm^2 compressive load. As a first approximation, we assumed that the interfaces would look like that illustrated in Fig. 2, open pores surrounded by GaAs/graphite hermetically sealed boundaries. With these assumptions, if the As vapor obeys the ideal gas law, the density of As molecules (either As_4, As_2, or some equilibrium combination), n/V, is given by

$$n/V=P/(RT),$$

where T is the annealing temperature (850 °C), R is the gas constant, P is the As overpressure (60 Torr), and V is the volume between the GaAs and graphite approximated by the volume of the graphite open pores. This analysis shows that to form a 60 Torr As overpressure, an average As surface concentration of $\approx10^{17}-10^{18}$ As/cm^3 is needed, which is consistent with secondary ion mass spectroscopy measurements in charged graphite holders. At 500 °C the equilibrium pressure of elemental As is somewhat less, ≈30 Torr.[12] This is still sufficiently high, however, so that one would expect a

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graphite holder charged at 850 °C to become fully ''discharged'' during an inert bakeout at 500 °C, as we observed. We also found that the graphite holders could be fully charged in a one-step process by annealing at 850 °C in contact with GaAs for a much longer period of time, on the order of 20 h instead of the 2 h period typically used for bonding.

Pyrolytic carbon-coated graphite was also investigated. As shown in Fig. 1, only one heat treatment was needed before the holder reached the fully charged state. This was probably due to the much lower surface porosity of the pyrolytically coated graphite as compared with uncoated graphite, thereby reducing the total amount of As required to charge the free volume of the open pores at the interface.

These experiments strongly suggested that the improvement of the transmittance of GaAs wafers with each successive use of the graphite holder is because graphite becomes charged with As and, therefore, retards the As loss from the wafers during bonding.

Next, the possible losses of As from the interface region to the furnace chamber were considered. Since graphite could be charged with As, it is reasonable to assume that the As diffusion through the bulk of the graphite holders was very slow. The self-diffusion coefficient of As in GaAs is vanishingly small, 10^{-27} cm^{-2} s^{-1} at 850 °C, and thus, a volume diffusion mechanism can be neglected. Arsenic diffusing out of the GaAs/graphite interface would have to pass through discontinuous pores and along the GaAs/graphite boundaries. Since boundary (surface) diffusion is much slower than vapor transport inside the free volume of the pores, the diffusion of As across the GaAs/graphite boundary must be the controlling mechanism.

The diffusion of As along the interface can be modeled by the following two-dimensional diffusion equation with the reference point at the center of the GaAs/graphite interface:

$$\frac{\partial C(x,y,t)}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} + D\,\frac{\partial^2 C}{\partial y^2},$$

where D is the diffusivity along the x and y axis.

The initial condition is

$$C(x,y,0) = C_i,$$

where C_i is the initial concentration. The boundary condition can be chosen as follows because the As partial pressure ≈ 0 in the furnace:

$$C(-a,y,t) = C(a,y,t) = 0,$$

$$C(x,-a,t) = C(x,a,t) = 0,$$

where a is the distance from the edge to the center of the GaAs/graphite interface. If we assume that D is in the 10^{-8} cm^{-2} s^{-1} range, a typical 2 h diffusion process could affect the As concentration within $\approx \sqrt{Dt} = 100$ μm from the edge of the sample. No difference in optical absorption was detected by Fourier transform infrared analysis between the center and the edge of the sample using a 2 mm diam beam, as shown in Fig. 1. It was, therefore, concluded that the actual diffusivity D must be less than 10^{-8} cm^2 s^{-1}. Very little As was thus expected to transport along the GaAs/graphite interface to the free surface.

The residual optical loss was found to be related to the surface roughness caused by the annealing process. This could be eliminated easily by repolishing.

The effect of the wafer quality and sample holder material (graphite, quartz, and sapphire) on optical loss in GaAs bonding has been investigated. Neither quartz nor sapphire could be used in contact with GaAs because of sticking at elevated temperatures. Graphite, however, did not stick to the GaAs wafers during the annealing (bonding) process. The transmittance of GaAs wafers was found to improve with successive uses of the graphite holder. After 1–3 uses, a state of maximum optical transmission was reached when the graphite became fully charged with As, which retarded the loss of As from the wafer during annealing. In the annealing process studies, which is the one used for wafer bonding (850 °C for 2 h), other features such as dislocation density (10^3–10^5 cm^{-2}), wafer orientation [(100) and (110)], and Cr dopant had little effect on the final optical loss. When semi-insulating GaAs wafers were bonded with an As-charged graphite holder at 850 °C, both bulk and surface optical absorption losses were low enough for practical high-power (QPM) (SHG) devices.

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