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TECHNICAL REPORT 1583(A)

THE CONSTRUCTION OF A DIFFUSED SEMICONDUCTOR LASER DIODE

Margaret Folkard

SUMMARY

This report describes some of the work undertaken by the author during a four months secondment to the Quantum Electronics Group of the Australian Post Office (now Telecom Australia) Research Laboratories in Melbourne. The secondment was arranged to provide an introduction to solid state device technology and to allow familiarisation with the methods of processing semiconductor material.

The various procedures necessary for fabricating the simplest type of semiconductor laser, that with a diffused homojunction in the III-V compound semiconductor gallium arsenide, were investigated and are reported here. Certain practical difficulties are also highlighted, and these must be resolved before more advanced devices can be achieved.

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The various procedures necessary for fabricating the simplest type of semiconductor laser, that with a diffused homojunction in the III-V compound semiconductor gallium arsenide, were investigated and are reported here. Certain practical difficulties are also highlighted, and these must be resolved before more advanced devices can be achieved.

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1. INTRODUCTION

This report describes some of the work undertaken during a period of secondment between April and July 1974 to the Quantum Electronics Group of the Telecom Australia Research Laboratories in Melbourne. The secondment was arranged to provide an introduction to solid state device technology and to allow familiarisation with the methods of processing semiconductor materials. The Quantum Electronics Group had already achieved some expertise in the processing of gallium arsenide light emitting diodes(ref.1) and were keen to extend this expertise to the production of semiconductor lasers. Consequently the various procedures necessary for fabricating the simplest type of semiconductor laser, that with a diffused homojunction, were investigated by the author and are reported here. The overall aim of the project was to gain experience in working with semiconductor materials, by making a gallium arsenide diffused homojunction laser from first principles.

With the advantages of hindsight, some of the specific processing problems which developed during the project might have been more efficiently approached using methods other than those detailed here. At the time the work was undertaken, however, the author had no previous experience in the semiconductor field and so the approach used, in the limited time available, was to follow on from the general processing techniques which had been used for the manufacture of light emitting diodes and vary these where necessary for the different requirements of semiconductor lasers.

Semiconductor lasers can efficiently convert direct electric current to coherent radiation. The wavelengths which may be emitted cover a wide range of the electromagnetic spectrum in the visible and near infrared regions, depending on which semiconductor material is considered. Although they are unable to provide the extremes of power and coherence which are available with gas and insulated rod type solid state lasers, their small size and low cost when integrated circuit techniques are used make the semiconductor laser worthy of detailed study.

Because semiconductor lasers are basically electronic devices with an output which can be modulated directly by the input current, they are well suited as radiation sources for integrated optical circuits. In particular, the diode laser offers great potential as a radiation source for long distance wideband communications using optical fibre transmission systems. Communications authorities are especially interested in the gallium arsenide transmitter, because it emits radiation characteristic of its bandgap energy at about 0.9μm. This wavelength is close to the spectral absorption minimum of commonly used optical fibres, and in addition is compatible with efficient silicon detectors.

2. THE SEMICONDUCTOR LASER

The semiconductor laser is a p-n junction in which lasing action occurs as the result of the stimulated recombination of carriers injected across the junction. Semiconductor lasers are generally made from direct bandgap materials, which have high electro-optic efficiencies because radiative transitions occur between states without the necessity of phonon interactions.

2.1 Principles of operation

Semiconductor lasers may be described as injection lasers, because current injection across a forward biased p-n junction is used to produce the population inversion necessary for lasing action to occur. The carriers injected across the junction diffuse some distance through the material before they recombine and lose their excess energy. This energy, which is approximately equal to the bandgap energy, can be released in a variety of

ways depending on the particular semiconductor and the doping levels involved. In gallium arsenide a high proportion of the injected carriers lose this excess energy by the emission of a photon.

In practice it is possible for holes injected into the n region to combine with electrons, and at the same time to have electrons injected into the p region, where they recombine with holes. The predominant process is determined by the relative impurity densities, the carrier lifetimes, and the carrier mobilities. Electron injection dominates in degenerately doped diodes, resulting in a region immediately to the p side of the junction where, because the population is inverted, luminescence is observed. The width of the light emitting region depends on the preparation of the junction, and decreases for high doping levels. The observed width of this region agrees approximately with estimates of the diffusion length for electrons in the p material; however it is also partly determined by dielectric waveguide effects caused by the variation of refractive index across the junction, because the active region has a slightly higher refractive index than the adjacent regions.

For low injection currents the photon emission is spontaneous, that is, electrons and holes recombine after a certain time without being affected by photons from other recombination events. This incoherent radiation is uniformly distributed across the junction and increases as the current is increased, until a certain current threshold is reached beyond which carrier recombination is stimulated by radiation from nearby events and the emissions become coherent.

Some directionality is usually imparted to the emitted radiation to promote lasing action. The most important laser structure is the Fabry-Perot cavity, (shown in figure 1) with two parallel reflecting faces perpendicular to the p-n junction, and the remaining faces deliberately roughened to prevent ordered reflections. This structure is readily achieved since gallium arsenide cleaves easily along the (110) planes and has a high refractive index ($n = 3.6$ at $0.84\ \mu$) which causes the semiconductor-air interface to act as a partial mirror and trap some of the radiation within the p-n junction region. If the diode current is made sufficiently large, an appreciable number of injected electrons will not have time to recombine spontaneously before being stimulated to emit photons with the same phase as the trapped photons. Amplification and further stimulated emission then occur in the flat p-n junction region. To achieve lasing action, more light must be produced by stimulated emission than is removed by photon loss processes such as absorption or scattering or leakage out of the end mirrors. Once this threshold condition has been reached, there is a great increase in intensity and a reduction in the linewidth of the emitted radiation.

In summary, then, the semiconductor laser is simply a p-n junction in the form of an optical resonant cavity which amplifies certain modes. Small variations in refractive index due to doping differences produce a waveguiding effect and so confine the emitted radiation to the plane of the junction.

The injection laser differs from a conventional solid state laser in that the former uses a diode which is by nature inhomogeneous, while the latter employs a homogeneous and optically perfect crystal. Typical characteristics of a semiconductor laser also differ from those of other lasers, because the discrete energy levels of the homogeneous solid are replaced by the broad conduction and valence bands typical of semiconductors. Thus many different electronic transitions can contribute to the energy of the lasing mode, making it difficult to achieve half-power spectrum widths less than 10Å, compared with linewidths smaller than 0.1Å for the other solid state lasers.

2.2 General requirements for the doping parameters

We need to consider the doping parameters which will produce a lasing diode having near optimum performance. In this work n type gallium arsenide substrate material was used and the p-n junction was formed by diffusion of the acceptor material, zinc.

The maximum photoluminescent efficiency in uniformly doped gallium arsenide occurs for acceptor and donor concentrations of the order of $10^{18}\,cm^{-3}$ at $77^{o}K$, increasing to $10^{19}\,cm^{-3}$ at $300^{o}K$. This surprisingly high doping level for the maximum efficiency condition has been explained as follows(ref.2). A constant number of non-radiative (defect) centres are believed to exist for a given sample with doping level less than approximately $10^{19}\,cm^{-3}$, while radiative electron-hole recombination is proportional to the majority carrier concentration. Therefore the relative rate of non-radiative recombination increases with decreasing doping level, resulting in decreased radiative efficiency. The sharp drop in radiative efficiency in the high doping range is explained by the formation of defects such as impurity precipitates, vacancy clusters, or vacancy-impurity complexes. Such defects increase with the doping level above $10^{19}\,cm^{-3}$ and result in non-radiative transitions.

Since diffused semiconductor lasers are generally operated at $77^{o}K$, the appropriate donor concentration N_D for optimum photoluminescent efficiency is of the order of $10^{18}\,cm^{-3}$. Polished wafers from Laser Diode Laboratories, n-doped with silicon to $1.5 \times 10^{18}\,cm^{-3}$, were used as substrate material in the work reported here.

For the type of diffusion that we are interested in, an acceptor impurity such as zinc is diffused into an n type substrate. Figure 2 shows the uniform donor concentration and the gradient in acceptor concentration which results from the diffusion. The junction occurs where acceptor and donor concentrations are approximately equal, at a depth which can be controlled by the diffusion conditions.

There appears(ref.3) to be a practical upper limit to the acceptor density which may be used, because for p concentrations greater than about $3 \times 10^{19}\,cm^{-3}$ (signified as p^{+}) a region of inefficient recombination occurs. This is probably due to structural damage caused by dislocations and crystal strains which increase scattering and absorption losses, and result in significant non-radiative recombination. By keeping the acceptor concentration throughout the material to less than $3 \times 10^{19}\,cm^{-3}$, this p^{+} region can be avoided. However the acceptor concentration must remain large enough to provide sufficient holes with which the injected electrons can recombine. A target figure for the acceptor concentration $N_A(0)$ at the surface was set at $2 \times 10^{19}\,cm^{-3}$.

2.3 Junction depth

In controlling the doping parameters we need to ensure that the depth of the junction below the surface is greater than the penetration depth of carriers injected across the junction. The penetration depth of carriers on either side of the junction is determined by carrier diffusion, which in turn depends upon the carrier mobilities and the minority carrier lifetimes. For the donor and acceptor concentrations used here, estimates of the diffusion lengths, L, lie within the range 1 - 5μ(ref.4,5,6). Sixty three percent of the injected carriers will be absorbed within a distance L from the junction, while in excess of 95% will be absorbed within a distance 3L.

As mentioned in Section 2.1, electron injection into the p region predominates for the usual doping conditions, which means that the active light emitting region will be on the p-side of the junction. The important dimension to consider is therefore the distance of the junction below the p-side metal contact. If the junction is too shallow, then electrons will be collected at the p-side metal contact before recombination can take place. If the junction is too deep, it is believed that a large number of injected electrons recombine non-radiatively in a thin region which reference 3 has claimed to exist immediately adjacent to the p-side of the junction. In this region, whose width increases with the junction depth, the hole concentration is very low and the radiative lifetime long. For deep junctions the width of this inefficient region will be appreciable, resulting in reduced radiative efficiency. It is therefore necessary to make a reasonable estimate for the optimum junction depth. From the foregoing discussion one would expect a suitable junction depth to be 2 or 3 diffusion lengths, and so a junction 10 μm below the substrate surface was aimed for.

2.4 The lasing cavity

A mesa structure was chosen for the lasing cavity because of the effect it has on reducing the threshold current. The large threshold currents which are necessary to initiate lasing action in a diffused diode, of the order of 100 KA/cm^2 at room temperature, cause significant heating effects. The rise in junction temperature reduces the diode efficiency and may lead to quenching of the laser action and even to destruction of the diode. By forming the metal contact to the p-GaAs as a stripe rather than a broad contact, the area of current injection into the junction is reduced, which results in a smaller lasing region. Although the current density should remain the same, the actual power input to the structure can be greatly reduced, with consequent reduction in heating effects. In practice it is found that leakage of both current and radiation occur from the region under the contact stripe. To maintain the current density in the plane of the junction at the required value, it thus becomes necessary to increase the current into the diode to compensate for current spreading. It is possible, however, to eliminate the spreading by removing the regions adjacent to the contact stripe, and forming a mesa about the p-n junction. Such a mesa construction produces lasers whose threshold current densities and efficiencies are quite close to those for conventional broad contact lasers, and results in significantly lower threshold currents.

2.5 Heat sinking and temperature effects

The operation of an injection laser is only possible if the junction temperature is kept below a critical value. Consequently, for a given power dissipated in the diode, the effectiveness of the heat sink is of considerable importance. In practice not all the pumping power supplied to a laser is emitted as light, a large proportion is converted into heat which raises the temperature of the junction. Heat is generated in injection lasers by both optical and electrical processes. The major optical sources of heat generation are non-radiative recombination of electrons and holes, and re-absorption of radiation in the inactive regions of the laser, while joule heating at the contacts is the major electrical source of heat generation.

If the temperature rise is large, then the electronic properties of the crystal may be altered sufficiently to prevent satisfactory laser operation. For diffused lasers having thresholds of the order of 100KA/cm^2 at room temperature, an enormous quantity of heat must be removed even for pulsed

laser operation. Both output intensity and wavelength are extremely temperature sensitive, and since most of the heat is created near the active region, a very efficient heat sink is needed to control the junction temperature and to stabilise the laser operation. If, as in stripe and mesa lasers, only a small area is activated by the injection current, then effective heat sinking is easier to achieve because less heat is produced.

3. PROCEDURE FOR FABRICATING A DIFFUSED HOMOJUNCTION LASER

Many different processes are involved in forming even the simplest type of diffused homojunction laser. This section considers the more important of these processes in broad outline, while Appendix 1 contains the specific details. The most common acceptor dopant for gallium arsenide reported in the literature is zinc, so this material was used in the present work.

3.1 Diffusion of zinc into gallium arsenide

Techniques for diffusing zinc into gallium arsenide obtain the necessary zinc vapour pressure from metallic zinc or from alloys of zinc and arsenic, or zinc and gallium. In this investigation metallic zinc was used. Gallium arsenide dissociates at the high temperatures needed for diffusion, so the diffusion must be carried out in an evacuated sealed silica ampoule. It is important to clean and degas the silica tubing and the diffusant because some impurities can cause considerable erosion of the substrate surface at elevated temperatures.

When the ampoule was placed for 2 minutes in the hot zone of a furnace which had been stabilised at a temperature of 1000°C prior to the introduction of the ampoule, the resulting diffusion produced a junction approximately 10 μ below the surface of the sample. In this case the acceptor concentration near the surface was of the order of $8 \times 10^{19} cm^{-3}$, which was much larger than the upper limit discussed in Section 2.2.

However if a silica film is deposited on the GaAs surface before diffusion, then the concentration of zinc is significantly reduced, producing approximately the level of doping required. The silica film serves the dual role of limiting the zinc concentration (and so reducing the junction depth) and of providing surface protection to the GaAs (hence allowing more planar junctions) by minimising thermal decomposition of the GaAs surface(refs.7,8). The silica film can be removed at the completion of diffusion by using a solution of hydrofluoric acid, buffered with ammonium fluoride to reduce the etch rate.

After the cleaning procedures described in Appendix 1, the substrates were coated with silica films from 2000Å to 6000Å thick. Two methods were available for the preparation of silica films, namely radio frequency sputtering or coating with an organic silicone solution.

Silica films sputtered from a high purity silica target in a radio frequency argon discharge are in principle preferred, however practical limitations of the equipment available for sputtering made these films unusable. In those regions where the silica films had been deposited uniformly, diffusion results were most satisfactory. The junctions so produced were extremely planar, and as shown in Table 1 for the example of diffusion at 1000°C, the junction depths were dramatically decreased. Junction depths were measured on the wafers, which were cleaved and stained in a solution

of HF : HNO_3 : H_2O = 1:3:4 for 30 s, then examined under high magnification with a Nikon microscope. Junction delineation is caused by the different etch rates for n-GaAs and p-GaAs.

TABLE 1.

Thickness of SiO_2 Film (Å)	Diffusion Temp. (°C)	Diffusion Time (min)	Junction Depth (μ)	
			Sputtered film	No film
1500	1000	45	9.3	160
3000	1000	60	9.7	190
5000	1000	60	4.6	180

The sputtered silica was deposited evenly over small regions, however most of the surface was covered with "pinholes" which allowed the zinc to diffuse through in an irregular manner. A junction produced in this way is shown in figure 3(a), while figure 3(b) illustrates the planarity possible in regions where the silica film is uniformly deposited. The "pinholes" in the sputtered silica film prevent the formation of a planar junction over the necessary areas, and so an alternative method of forming a silica barrier layer was examined.

The other method used for producing silica films which had been used during the processing of light emitting diodes, was to spin on an organo-silicone solution (Emulsitone " Silicafilm") using the Headway spinner model AHT1-T54. The spun silica film was air-dried for 30 min under laminar flow conditions, then baked at 200°C for a further 2 hours before diffusion. The junctions produced after diffusion were much deeper than for the same thickness of sputtered film, as can be seen by comparing Table 2 with Table 1 . (Teede(ref.1) found that when zinc was diffused through spun silica films the junction depth varied only slightly for silica film thickness greater than 2000Å). In addition, as shown for a typical case in figure 4, the diffusion fronts were so irregular, that in all cases studied, the junctions were not sufficiently planar to be of use for laser fabrication. (However as reported in reference 1, these irregular junctions can produce good light emitting diodes, for which junction planarity is relatively unimportant).

TABLE 2.

Thickness of SiO_2 Film (Å)	Diffusion Temp. (°C)	Diffusion Time (min)	Junction Depth (μ)	
			Sputtered film	No film
1500	1000	60	39 ± 5μ	170μ
2000	1000	60	28 ± 5μ	170μ

Since neither spun nor sputtered silica films produced sufficiently planar p-n junctions, the majority of diffusions were carried out on gallium arsenide substrates which had no protective film whatever. Thermal decomposition of the unprotected substrate surface later caused many problems in the photolithographic processing, and is the major problem to be overcome before lasers can be successfully fabricated in this manner. A particularly badly affected surface is shown in figure 5, however figure 6 demonstrates that planar junctions are still possible despite the surface deterioration. In general, flatter p-n junctions are obtained from diffusions at 1000°C than from diffusions at 850°C, where a longer diffusion time is required to achieve the same junction depth. Acceptor concentrations higher than our target figure are obtained when diffusion occurs without a protective film. Although these high p concentrations will cause a reduction in diode efficiency, there are some minor compensations for this in that fabrication of an ohmic low resistance contact is facilitated as the p doping becomes increasingly degenerate.

All substrates used for diffusion were placed in a 6 mm i.d. Spectrosil silica tube which had previously been cleaned in aqua regia then rinsed in distilled deionized water and methanol. After etching in hydrochloric acid, a small quantity of high purity zinc was loaded into the tube which was then evacuated to less than 10^{-5} torr before sealing. Two milligrams of zinc were sufficient to supply the equilibrium vapour pressure in the 2 - 3 cm^3 ampoule at 1000°C, but in later runs less metal was used with the aim of minimising surface deposits on the substrate. The oven was brought up to the diffusion temperature of 850°C or 1000°C and stabilised before inserting the ampoule. At the completion of the diffusion period, whose time depended on the temperature and whether a silica film was present or not, the ampoule was extracted from the hot zone of the oven and the diffused wafers were removed from the ampoule for evaluation and device fabrication.

When no protective silica film was present, the diffusion frequently resulted in a dull surface on the previously polished GaAs. This dull layer could not be removed by concentrated HCl or H_2SO_4, or by boiling in any of the reflux cleaning solvents. In the subsequent photolithographic stages it often caused problems because the spun-on silica films and photoresist layers would not adhere properly to the uneven surface, and at some time during the extended processing would tend to lift off in patches. This would then allow etching of the silica or gallium arsenide to take place in regions where such etching was not at all desirable.

When a protective silica barrier had been present on the GaAs surface before diffusion, the silica film plus any zinc on top could be readily stripped using buffered hydrofluoric acid solution. This then left a clean polished substrate surface which caused no problems in subsequent photolithographic processing. However, as already noted, the p-n junctions under these conditions were not sufficiently planar over extended regions to form lasing cavities.

The hole mobility and carrier concentration in the diffused material were measured after preparation of the sample. The silica film, if present, was removed using a buffered hydrofluoric acid solution, the p layer which had diffused through the unpolished side of the wafer was ground away, and six metallic contacts were vacuum evaporated onto the polished p surface. The conductivity of the p layer was determined and the mobility found from the Hall effect. These parameters then allowed determination of the p dopant concentration. A typical 2 minute diffusion at 1000°C into a gallium arsenide surface not protected by a silica film was found to produce an average p concentration of 8 - 10 x 10^{19} cm^{-3} and a p-n junction 9 - 10 μ below the surface.

3.2 Photolithographic processing

The photolithographic procedures outlined in this section are the steps which were used to define the active region of the laser, isolate it from the main body of the GaAs substrate and allow the laser units to be separated from one another ready for mounting on heat sinks. Appendix 1 contains further details of each process.

In cases where a silica film had been present during diffusion, this was afterwards stripped by immersion in a buffered hydrofluoric acid etch. A fresh silica film about 5000Å thick was applied using the organic silicone solution which was air-dried and then baked to obtain the hardness needed during later processing. Shipley positive photo-resist type AZ1350H was applied through a millipore filter to the surface of the wafer, which was then spun, air-dried and baked. After these drying steps, the wafer was exposed through the appropriate master photographic plate for 25 s in a Karl Zuss aligner model MJB J11 KSM, then baked before development. The baking process hardened the photoresist so that it would mask against all chemicals used in subsequent etching. The baking times were varied in an effort to obtain better masking, however if baked for longer than 15 min the photoresist became exceedingly difficult to remove using the recommended remover (Shipley Type JJ32).

The pattern for the photolithographic plates had been formed on "Cut and Strip" Rubylith Mylar by a co-ordinatograph, 70 times greater than its final size. The pattern was photographed in two stages using a Klimsch camera which had a lens with a resolution of 200 line pairs/mm. The initial reduction of 3.5:1 was followed by a reduction of 20:1, giving the final mask pattern size of 6 mm x 10 mm, which was set on 4 in x 5 in glass photographic plates.

The exposed wafer was developed for 40 s in a 1:5 solution of Shipley Photoresist developer type KC90 in water. This step exposed the silica film in areas where it was to be removed. Where the photoresist had been removed, 3 min immersion in buffered hydrofluoric acid was sufficient to etch through the silica film to the surface of the underlying gallium arsenide. The normal procedure at this stage would be to remove the photoresist by a 2 min immersion in a 1:2 solution of Shipley Remover type JJ32, followed by placing the wafer in gallium arsenide etching solution. However, if this procedure was followed, then the etching solution tended to attack portions of the wafer which were supposedly protected by the silica film. If the wafer was placed in the GaAs etchant before the photoresist was removed, then excellent etching definition was achieved. However, in this case the photoresist itself became exceedingly difficult to remove, with incomplete removal of the hardened photoresist causing major surface problems in subsequent photolithographic processing.

A variety of gallium arsenide etchants were investigated, including mixtures of sulphuric acid, hydrogen peroxide and distilled water in various proportions, and solutions of bromine in either ethanol or methanol. With most etchants a significant undercutting of gallium arsenide takes place below the silica mask, which greatly increases the difficulty of some of the later photolithographic processing steps. An interesting effect was observed with the bromine-methanol etchant. If the mask was aligned parallel to the (110) reference edge of the gallium arsenide substrate then substantial undercutting occurred. However when aligned normal to the (110) reference edge, the etch rate was greatly increased, very little undercutting occurred and a V-section was formed. The difference in etching effects is clearly shown in figure 7. This effect was not observed with bromine-ethanol or the various sulphuric acid - hydrogen peroxide-water mixes, for which the slower etch rate and amount of undercutting were independent of substrate

orientation. Following these observations, bromine-methanol etches were chiefly used. When applied to an etch pattern running normal to the (110) edge of the substrate, a 5% solution produced an etch rate of approximately 7 μm/min at room temperature. The etch rate was reduced to 3 μm/min for a pattern exposed parallel to the (110) edge. The 5% solution was found to be too violent in its effects on the gallium arsenide substrate, and 3% and 1% solutions were later substituted.

Three separate masks were used, each with an image 6 mm x 10 mm. Mask 1 was the most complicated, with a pattern of clear and dark stripes whose sequence was repeated every 420 μ, the basic width of each laser unit. The pattern on mask 1 was used to produce a mesa structure on the substrate surface, while mask 2 with 70 μ clear stripes repeated every 420 μ, was used to separate the individual laser units from each other. Mask 3, which had 30 μ clear stripes repeated every 420 μ, was used to allow electrical contact to the mesa stripe without allowing electrical contact to the supporting structure.

3.3 Electrode contacts

Contacts between gallium arsenide and most metals are ohmic at high carrier concentrations, although the metal-semiconductor resistance may become appreciable. Contact resistance is particularly important for the p-contact in highly doped stripe-geometry diodes where the contact area is small and the injection currents are large.

A method for forming reproducible n and p metal contacts to gallium arsenide light emitting diodes had been developed by Teede(ref.1). This procedure, in which a number of elemental metals were simultaneously vacuum evaporated from a tungsten source, was used in the present work. For the source and substrate holder used here, 130 mg of metal when totally evaporated produced a film approximately 3000Å thick. The p contact was formed from a mixture of 96% silver and 4% manganese, while the n contact used 84% gold, 12% germanium and 4% nickel. Adhesion of the metal to the gallium arsenide surface was poor, but after alloying under flowing hydrogen, the contacts became much stronger and quite reproducible.

3.4 Formation of the laser cavity

After metallising and alloying the p and n surfaces, the wafer was cleaved along (110) planes at intervals which depended on the desired length of the laser cavity. In the present work, cavity lengths generally ranged from 300 μm to about 500 μm. The cleaved faces act as laser end-mirrors, because the coefficient of internal reflection of about 35% at the semiconductor-air interface allows sufficient feedback for lasing action to develop. The individual lasers were next separated by cracking along the etch lines formed by photolithographic mask 2, shown in figure 8. For the set of masks used here, each individual laser unit had a total width of 420 μm, while the contact stripe on the mesa was 30 μm wide.

3.5 Heat sinking

To heat sink the diodes fabricated in the present work, they were bonded n-side down to gold coated copper headers using a thin layer of gold-tin alloy. The 80% gold-20% tin eutectic alloy has a melting point of 280°C, so above this temperature it could be spread on the header under a mixture of 5% hydrogen in nitrogen. Alternatively, a 0.001 inch thick preform wafer made of the gold-tin eutectic was placed between the n side of the diode and the gold header heat sink, which was clamped to a resistance heater. Passing a current of 2.5 A at 50 V through the oxidised nichrome wire around the clamp melted the gold-tin preform and bonded the laser

directly to the header. For efficient contacting, the diode was held in a vacuum holder and then pressed onto the header with a pressure of about 3000 lb/in^2, which is about 20% of the fracture strength of GaAs(ref.9). The gold header, which was very large compared to the laser diode, then became an effective heat sink.

4. CONCLUSION

Useful experience was gained in all the individual processes necessary for fabricating diffused homojunction laser diodes, although no operating devices were obtained in the limited time available.

The main difficulty lay in adequately protecting the substrate surface during its elevation to high temperatures during diffusion. If no protective film was applied to the substrate surface before diffusion, the p-n junctions were usually adequately planar to allow lasing action to develop but the damaged substrate surface made subsequent photolithographic procedures very difficult. Both available methods for applying a protective silica film to the substrate surface resulted in junctions which were insufficiently planar to form lasing cavities, although the R.F. sputtered film produced highly planar junctions over the limited region between "pinholes".

Before successful devices can be made, further effort must be applied to develop a protective film which will deposit uniformly over the substrate surface. If the "pinhole" density can be reduced, perhaps by paying greater attention to the elimination of contamination within the sputtering chamber, then planar p-n junctions and undamaged substrate surfaces will result. The general techniques for materials processing which have been outlined in this report should then permit the successful fabrication of diffused semiconductor lasers.

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APPENDIX I

SUMMARY OF PROCESSES FOR FABRICATING A DIFFUSED HOMOJUNCTION SEMICONDUCTOR LASER DIODE

I.A Diffusion steps

1. Cut and polish slices of monocrystalline GaAs.
2. Scribe and break GaAs slices into wafers 6 mm x 10 mm, the longer side normal to the (110) reference edge.
3. Clean wafer progressively in boiling reflux solutions of acetone, methanol, 20% hydrochloric acid, distilled water, and ethanol.
4. Coat with protective barrier of silica film, several thousand angstroms thick.
5. Place coated wafer and cleaned metallic zinc in a silica tube and evacuate.
6. Seal silica ampoule and place in the pre-heated furnace for the desired diffusion time.
7. Cleave a slice from the end of the wafer and use this to determine the junction depth by immersing the slice in a junction delineation etch $HF:HNO_3:H_2O = 1:3:4$ for 15 - 60 s.
8. Evaporate point contacts onto a small sample of the wafer and determine the average p concentration using the Hall effect.

I.B Photolithographic processes

9. Apply silica film. Use radio frequency sputtering or spin coat. For the latter, spin coat p side of wafer with silica at 4000 rev/min for 25 s. Dry under laminar flow for 30 min, then bake at 200°C for 2 hours.
10. Spin coat with photoresist at 4000 rev/min for 2 s. Dry under laminar flow for 15 min, then bake at 40 - 50°C for 15 min.
11. Expose through mask 1 to ultraviolet light for 25 s in the mask alignment system.
12. Bake at 120°C for 15 min.
13. Develop for 40 s in 1:5 solution of photoresist developer in distilled water (this step removes exposed photoresist).
14. Etch unprotected silica in buffered hydrofluoric acid solution for 3 min.
15. Remove unexposed photoresist, leaving protective silica film.
16. Etch unprotected GaAs with 3% bromine-methanol solution (or other etchant as desired).
17. Remove silica film with buffered hydrofluoric acid.
18. Repeat steps 9 to 17, now exposing the wafer to ultraviolet light through mask 2, after aligning mask 2 with the etch lines from mask 1.
19. Repeat steps 9 to 15, now exposing the wafer through mask 3 after aligning mask 3 with the etch lines from masks 1 and 2 (Note: when using mask 3, no etching of GaAs takes place, only etching of the silica film).

I.C Deposition of metal contacts

20. Vacuum evaporate p metal contact Ag:Mn = 96:4 and alloy at 550°C for 2 min under H_2 flowing at 2 l/s.

21. Grind away diffused p layer on back unpolished surface, then grind n layer to desired thickness using mechanical polishing.

22. Vacuum evaporate n metal contact Au:Ge:Ni = 84:12:4 and alloy at 450°C for 20 s under flowing H_2.

I.D Mounting of individual laser units

23. Scribe and cleave wafer along (110) planes to form laser mirrors at intervals depending upon the desired lengths of the laser cavities.

24. Break along deep etch lines 420 μ apart, (normal to (110) plane) to separate into individual laser units.

25. Mount on individual heat sinks and make electrical connections with thin gold wires.

I.E Characterisation of individual lasers

26. Test light output and current characteristics as a function of bias voltage applied across the diode.

27. Test capacitance characteristics as a function of reverse bias voltage in order to determine the doping profile.

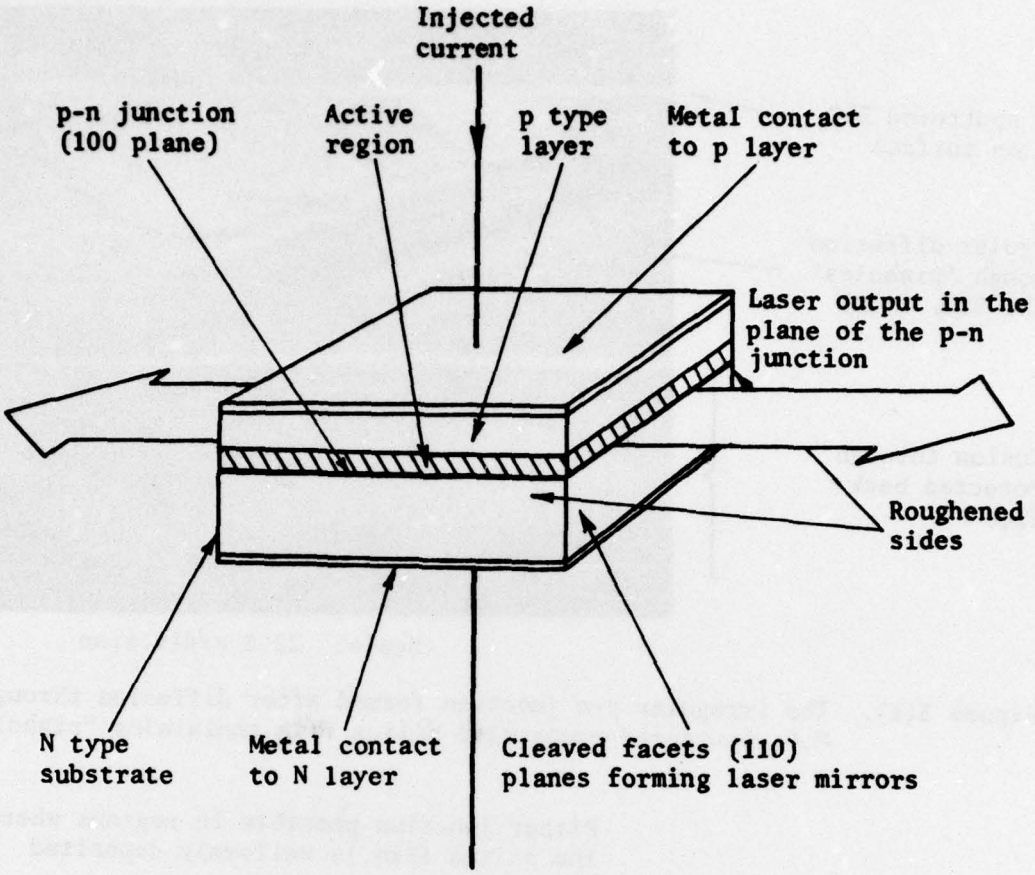


Figure 1. Schematic of the semiconductor diode laser

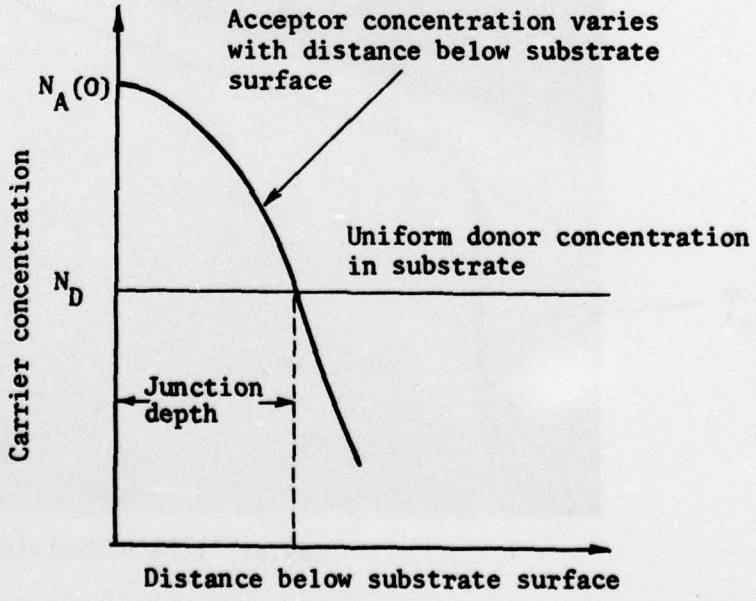
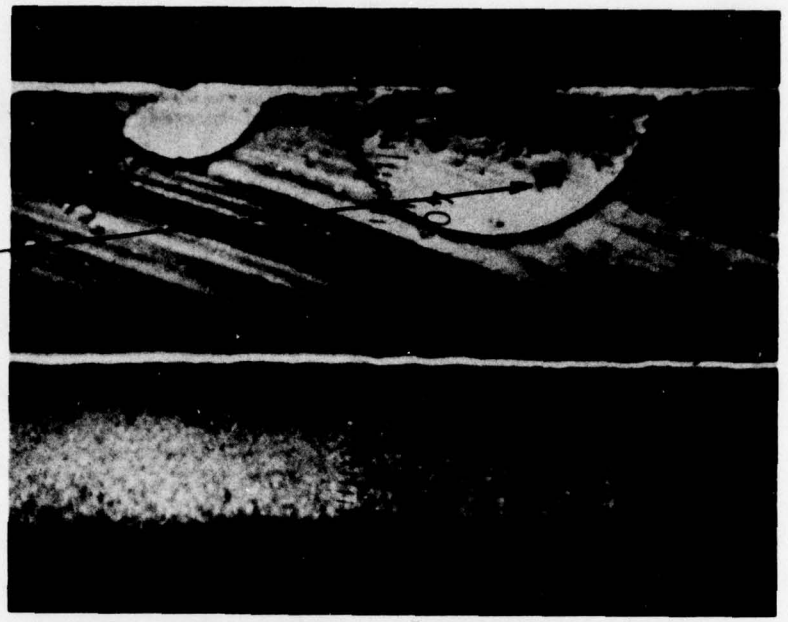
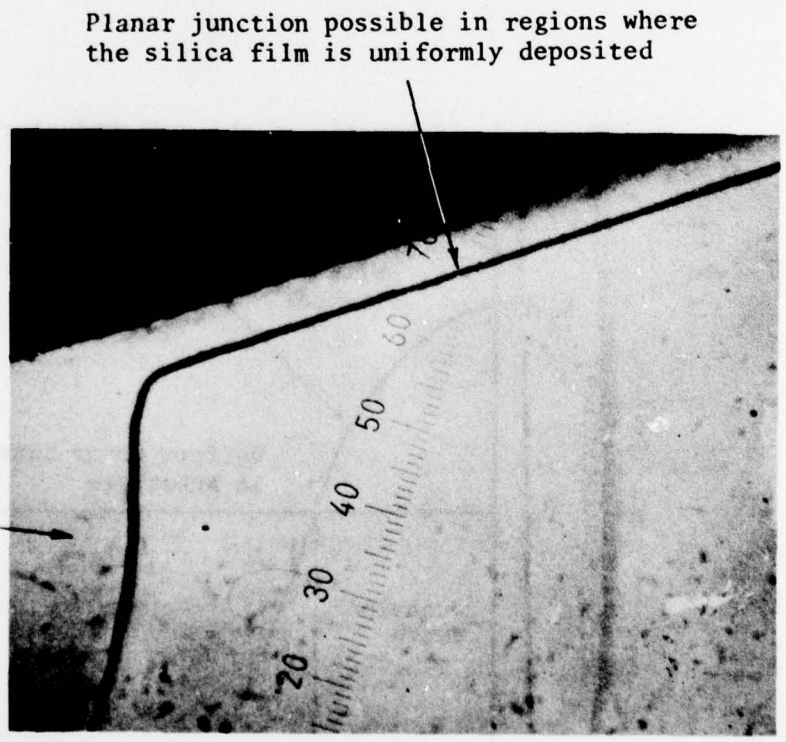


Figure 2. Doping concentration profiles for an acceptor diffused into a uniformly doped n type substrate



Scale: 22.8 μ/division

Figure 3(a). The irregular p-n junction formed after diffusion through an R.F. sputtered protective silica film containing "pinholes"

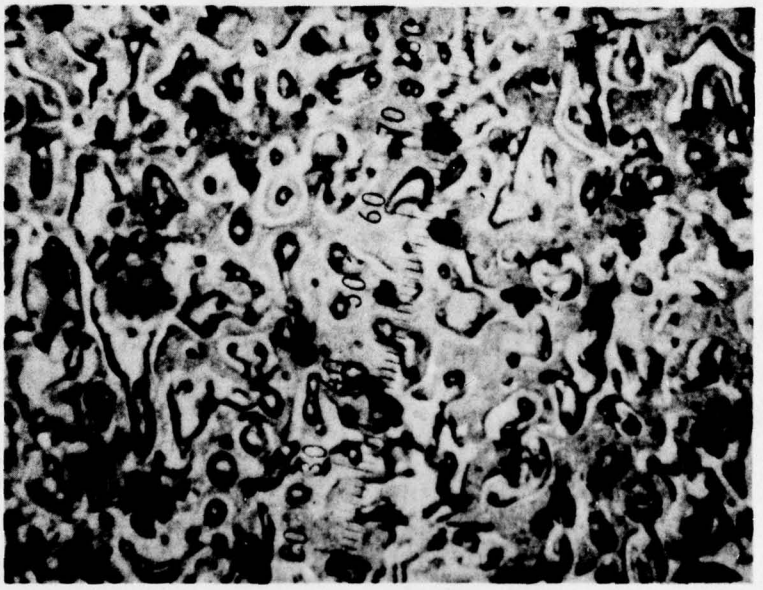


Scale: 1.73 μ/division

Figure 3(b). The p-n junction formed by diffusion through an R.F. sputtered silica film

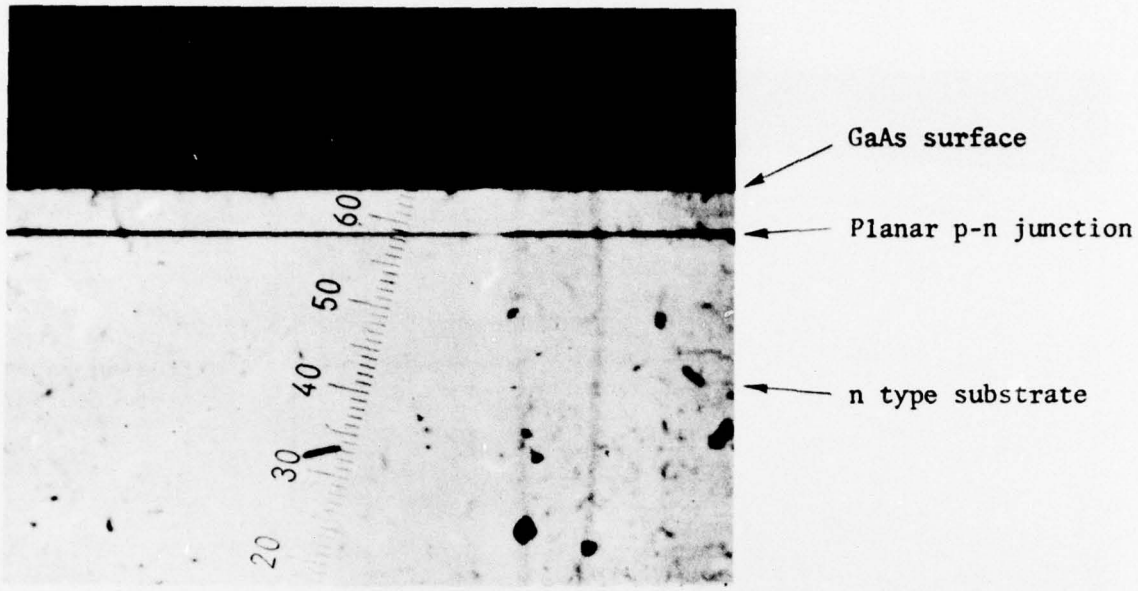
Scale: 22.8 μ/division

Figure 4. The p-n junction formed by diffusion through a "spun" protective silica film



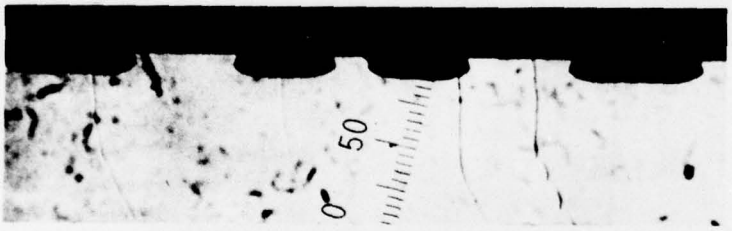
Scale: 1.73 μ/division

Figure 5. A badly affected surface after diffusion when no protective silica film is present



Scale: 1.73 μ/division

Figure 6. The p-n junction formed by diffusion when no protective silica film is present. (Diffusion at 1000°C for 2 minutes)



significant undercutting below the mask

(a) mask pattern aligned parallel to to (110) reference edge

greatly reduced undercutting below the mask

Scale: 6.5 μ/division

(b) mask pattern aligned normal to (110) reference edge

Figure 7. Selective etching of gallium arsenide with a solution of 5% bromine in methanol

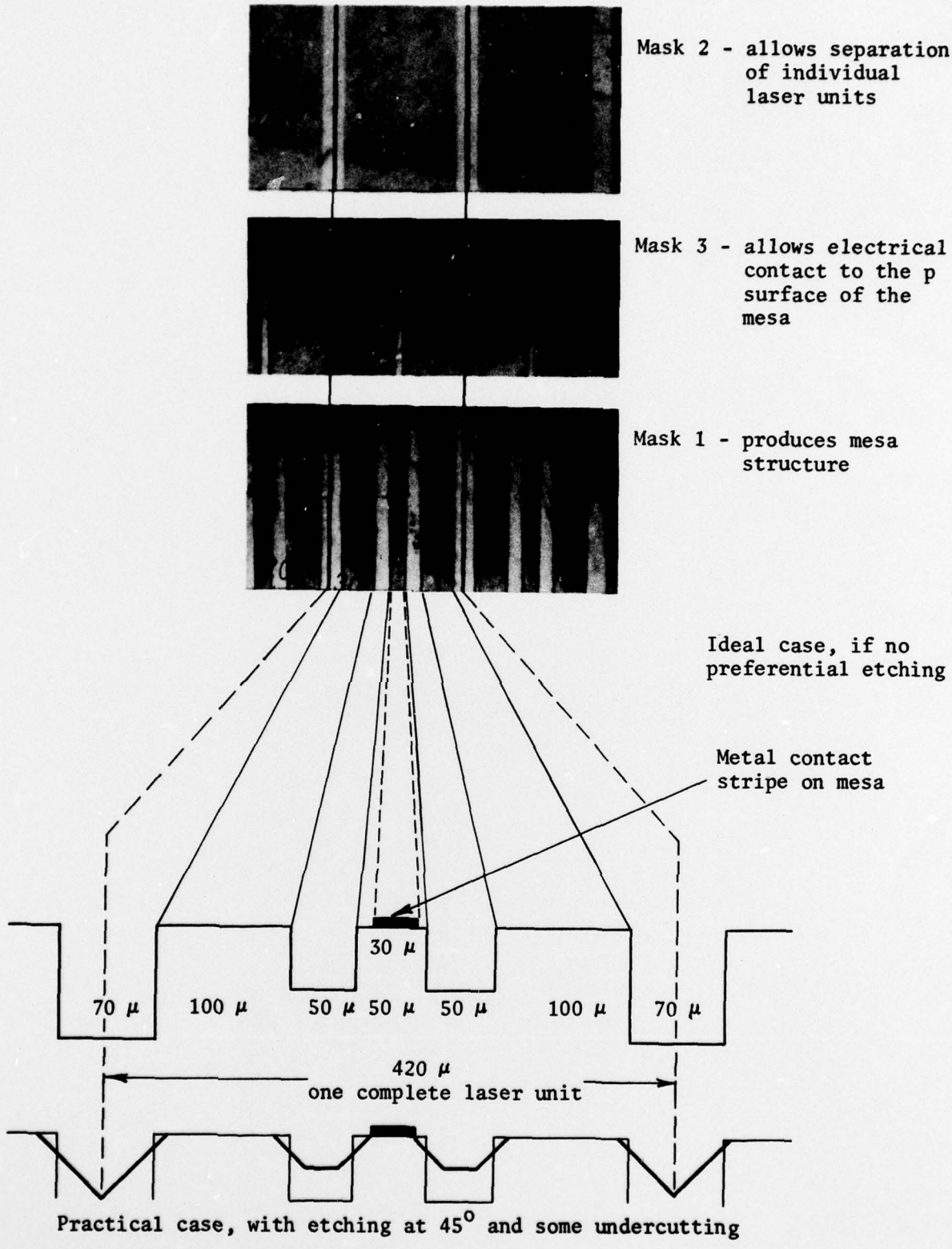


Figure 8. Photolithographic masks used to produce mesa stripe lasers from a diffused substrate wafer

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