n_e as long as the gas temperature remains low. However, the strong detrimental effect of rising gas temperature on α_0 causes the optical power density to decrease with increasing temperature in spite of the increase in saturation intensity. The optical power density approaches zero even for values of electron density in excess of 10^{10} cm⁻³ if the gas temperature is greater than approximately 700 °K. These results clearly indicate that merely increasing the discharge power (essentially proportional to n_e) for a CO_2-N_2-He laser mixture will not yield an increase in laser output if the power increase is accompanied by a significant elevation in gas temperature. Gas temperature is therefore seen to be the most important plasma property in determining CO_2 electric discharge laser performance.

Under typical experimental conditions, the electron density and average energy and the gas temperature are subject to radial and/or axial gradients, and any experimental measurement of the laser properties of the discharge will be affected by these gradients as well as by the extent of CO_2 dissociation which is known to be important to laser performance.[17] Therefore, ultimate verification of the calculated results presented herein awaits carefully controlled measurements in which these factors are taken into account.

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LOW-TEMPERATURE MIGRATION OF SILICON IN THIN LAYERS OF GOLD AND PLATINUM*

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The backscattering method is employed to obtain microscopic information about solid-solid reactions of Si with thin layers (500—2000 Å) of both vacuum-evaporated Au and sputtered Pt. A remarkable observation is the migration of Si atoms into Au and Pt at relatively low temperatures (150 and 350 °C, respectively). Migration of Si in Pt induces first the formation of Pt_2Si-like compounds and then PtSi. In the Au-Si system, on the other hand, Si moves through and accumulates on the Au surface in the form of SiO_2 under an oxidizing heat-treatment atmosphere.

The formation of contacts by metals such as aluminum, gold, and platinum with silicon has been investigated repeatedly and primarily because of the industrial interest in Ohmic contacts to n- and p-type silicon.[1] The remarkable finding is that permanent contacts are formed at temperatures far below that of the eutectics. For example, platinum silicide (PtSi) can be formed at around 400 °C, while the eutectic temperature is 980 °C. Information on the microscopic processes of these solid-solid reactions is essentially nonexistent in the literature. Backscattering is an ideal tool to ana-

FIG. 1. Energy spectra of 2-MeV ^{4}He$^+$ ions backscattered from a randomly oriented silicon single crystal covered with 900 Å of vacuum-evaporated gold after (1) 2 weeks of storage at room temperature, (2) 20-min anneal at 150 °C in air, and (3) 20-min anneal at 200 °C in air. The dotted line is the spectrum of an uncovered silicon sample. The shift of the leading edges in the gold and silicon spectra is produced by the growth of a SiO$_2$ layer over the gold surface.
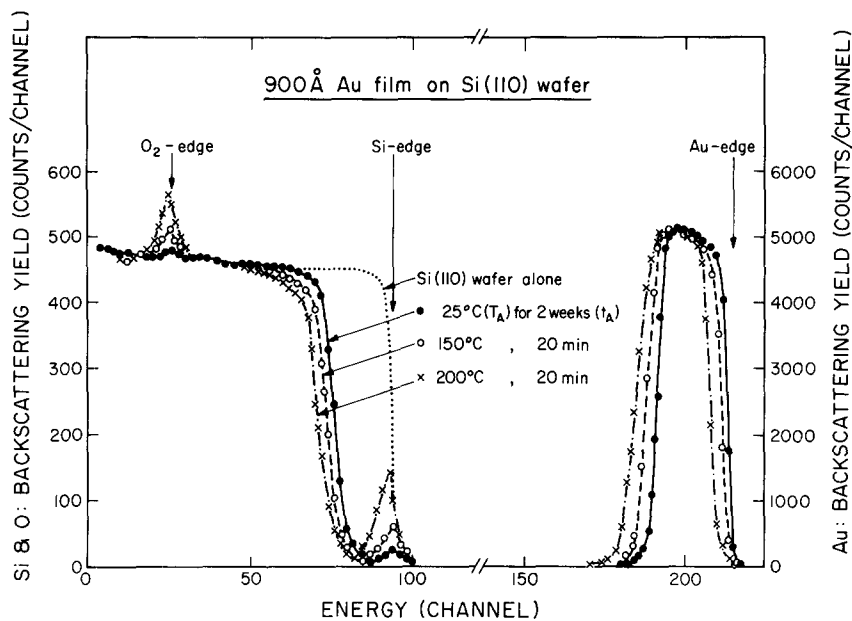
lyze this kind of phenomena occurring within depths of 100–5000 Å below the surface of a solid substrate.[2] We have applied this technique to investigate the low-temperature processes in the Au-Si and Pt-Si systems and found migration of silicon atoms into both metal films at temperatures well below that of the eutectic.

The platinum films were 500 and 2000 Å thick and produced by standard low-energy sputtering techniques on a {111} surface on n^+-type silicon.[3] The gold films ranged from 200 to 1000 Å and were obtained by vacuum evaporation on p-type silicon wafers oriented in a ⟨110⟩ direction. The surface was prepared by conventional mechanical and chemical polishing, after which the sample was kept under diluted hydrofluoric acid until just before evaporation. Backscattering data were obtained with the 3-MV accelerator at the Kellogg Laboratory of the California Institute of Technology.

When such a silicon wafer covered with gold is heated in air to about 150 °C the following facts are observed: (1) silicon atoms migrate through the gold film and accumulate on its front surface, (2) the accumulated silicon is chemically bound in the form of an oxide layer, (3) the major growth of the layer takes place within the first 10 to 15 min of the heat treatment, and (4) the thickness of the layer increases with increasing temperature of the treatment. The process is associated with a visible change in the color of the surface; the final appearance depends on the heat treatment and the gold thickness. This migration of silicon through gold takes place well below the eutectic temperature, since the Au-Si eutectic lies at 370 °C.

These conclusions are drawn from the results of backscattering experiments. A typical spectrum is shown in Fig. 1 where the backscattering yield of 2-MeV ^{4}He$^+$ ions is plotted as a function of the energy of the scattered ions (∝ channel number) for a random crystal orientation. The three curves correspond to three different samples obtained from the same gold-evaporated wafer after (1) 2 weeks storage in room ambient, (2) 20-min anneal at 150 °C in air, and (3) 20-min anneal at 200 °C in air. Also shown is the yield obtained from a silicon wafer without a gold layer (dotted curve). The figure indicates that the heat treatments induce an accumulation of silicon at an energy corresponding exactly to the open silicon surface of the reference sample. Simultaneously, there is a build-up of oxygen at the surface indicating the formation of a silicon oxide layer. The areas under the silicon and oxygen peaks correspond within statistical errors to a composition of SiO$_2$. Also, the gold spectrum shifts to slightly lower energies, as expected from the energy loss introduced by the silicon oxide in front of the gold. No change is observed in the profile of the gold spectra. This indicates that no noticeable migration of gold is taking place at these low temperatures. It also proves that the silicon accumulates as a uniform oxide layer over the gold. Similar remarks apply to the shift of the silicon edge of the substrate. The shifts of the gold edge and the silicon edge are equal in magnitude; an analysis indicates that they should indeed be so for a layer of SiO$_2$ over the gold surface. Oxide layers as thick as 2000 Å have been obtained at 250 °C. The amount of silicon oxide which grows during the heat treatment depends on the ambient
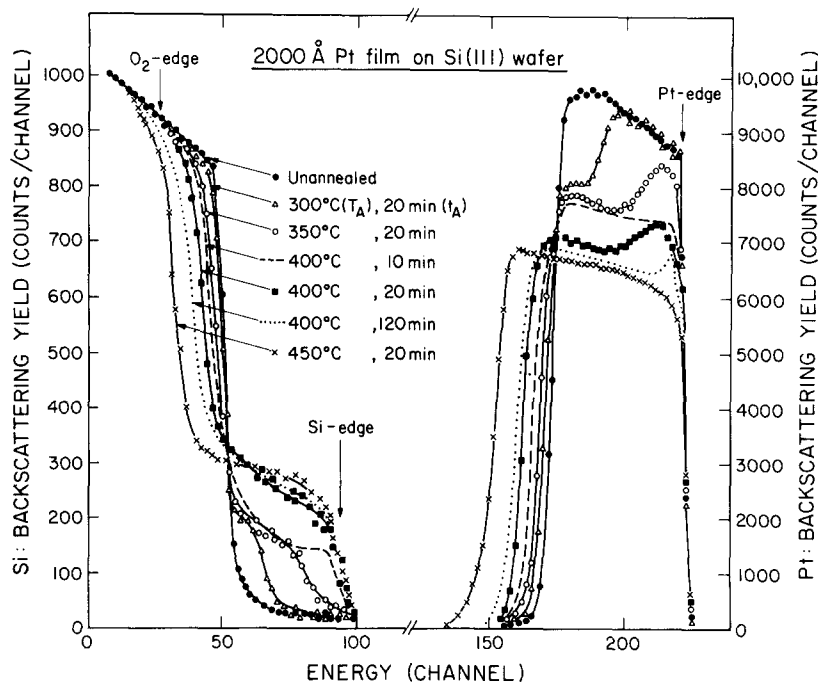
FIG. 2. Energy spectra of 2-MeV $^4He^+$ ions backscattered from a randomly oriented silicon single crystal covered with 2000 Å of sputtered platinum after various anneal treatments. For the dashed line (400 °C, 10 min), the ratio of the yields corresponds to Pt_2Si; for the crosses (450 °C, 20 min), this ratio corresponds to PtSi.

atmosphere. Air enhances the process when compared with a nitrogen atmosphere. Further support is obtained when a wafer treated at 150 °C is dipped into hydrofluoric acid. The whole spectrum returns to that found prior to annealing. At temperatures above 250 °C but still below eutectic, gold begins to penetrate into the silicon.

Corresponding experiments with platinum films yield somewhat different results, as shown in Fig. 2. At 300—350 °C a front of silicon is seen to progress into the platinum. How deep the silicon penetrates depends both on anneal duration and on temperature. The ratios of the corresponding silicon-to-platinum yields indicate that Pt_2Si-like compounds are formed by the migration of silicon into the platinum film.[4] This process can be carried to the limit where a layer of uniform composition is obtained (dashed line, at 400 °C for 10 min). If either the anneal temperature or the anneal duration are increased, the layer transforms to the thermodynamically stable composition PtSi (dotted line, at 400 °C for 2 h).[5] The platinum spectrum widens because the added silicon changes the composition and the width of the layer. When the spectra are transformed from an abscissa of energy to one of depth, taking into account the change in stopping power, the final PtSi layer is found to be twice as wide as the original platinum layer. This agrees well with the crystallographic data of the two substances.

Figure 2 shows that the leading edge of the platinum spectrum does not shift, and that no accumulation of silicon takes place on the front surface. This was found for both annealing in air and nitro-

gen atmospheres. The low-energy spectrum reveals no build-up of surface oxygen either. No significant amount of silicon oxide is thus formed over the PtSi film. Further anneal up to 600 °C does not produce any noticeable changes in the spectra. This contrasts with our observations on gold films and is possibly related to the existence of stable compounds of silicon and platinum.

We have observed that silicon migrates through thin layers of gold and platinum at temperatures well below that of the eutectics.[6] In platinum, the existence of a stable-compound PtSi determines the final thickness of the layer. This fact offers reproducibility for Ohmic contacts in industrial applications because the final thickness of the layer is determined by the initial thickness of the platinum film. On the other hand, the amount of silicon that migrates through the gold film depends on both temperature and atmosphere. At temperatures above 250 °C gold also migrates into the silicon. These effects probably form the basis for thermal-compression bonding.

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[4]Backscattering cannot distinguish *a priori* between

migration of Si into Pt or vice versa. However, the long leading edge in the silicon spectra (e.g., at 350°C) and the fact that initially thermodynamically unstable platinum-rich compounds are formed suggested that silicon is the migrating species.

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[6]We speculate that low-temperature migration may be a common phenomenon in systems where compounds and/or eutectics exist. Further investigations on a range of systems are under way.

POWER AND LINEWIDTH OF TUNABLE STIMULATED FAR-INFRARED EMISSION IN LiNbO3[†]

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The power-versus-wavelength characteristic for a high-power, continuously tunable far-infrared source has been experimentally determined and compared with theory. Utilizing a Q-switched ruby laser as the pump and stimulated polariton scattering in the crystal LiNbO3 as the scattering mechanism, peak powers outside the crystal of ~ 3 W at $200\,\mu$ are observed without crystal damage. Linewidth measurements indicate a bandwidth of < 0.5 cm^{-1} for the radiation over the observed tuning range 66–200 μ.

We recently reported the direct detection of tunable stimulated far-infrared radiation accompanying optical scattering from the lowest A_1-symmetry polariton mode in LiNbO3.[1,2] The stimulated radiation results from a parametric process whereby input pump photons of frequency ν_p interact with an optical vibrational mode in the crystal at frequency ν_i, producing "signal" radiation at $\nu_s = \nu_p - \nu_i$ and "idler" at ν_i. Since the idler frequency and wave vector must lie on the material dispersion characteristic (ω-k diagram), a unique set of allowed frequencies and wave vectors is determined for the scattering process.[3] Simultaneous tuning of signal and idler is then accomplished by varying the angle between pump and signal propagation vectors.

In our experiment, opposite ends of an uncoated a-axis LiNbO3 crystal were polished flat and parallel to form a low Q resonator for the signal radiation. Tuning was accomplished at room temperature by mechanically varying the angle between the pump beam and the crystal surface normal. The pump, signal, and idler are linearly polarized parallel to the crystal c axis.

The experimental arrangement is shown in Fig. 1. The pump was a Q-switched ruby laser (6943 Å) emitting 20-nsec pulses with a peak power of 6 MW and a beam diameter at the laser of about 2 mm. The experiment was performed on a "single shot" basis, but pulse repetition rates of up to 1 pps are possible with our present laser system. A 50-cm focal length lens focused the beam near the output end of a 3.4-cm a-axis LiNbO3 crystal with the laser polarized along the c axis. The laser lens combination is mounted on a rotatable

bench with its pivot point coinciding with the output end of the crystal which rests on a fixed platform. The end faces of the crystal were polished flat and parallel to within a few seconds of arc. In addition, a cut was made in the corner of the crystal output end at the proper angle to allow the idler radiation to emerge approximately normal to the exit surface and, hence, minimize reflection loss at the crystal-air interface. Infrared detection was provided by a calibrated Golay detector system, with a black polyethelyne filter placed in the collecting light pipe to eliminate opti-
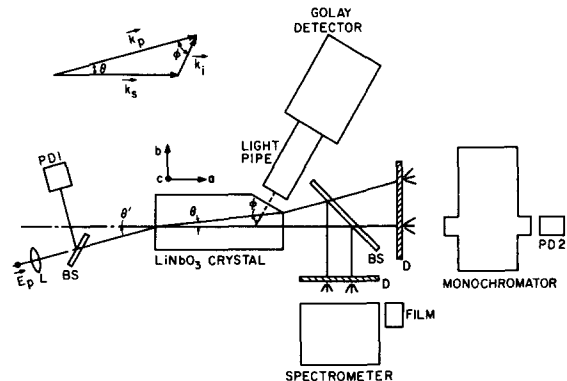

FIG. 1. Schematic diagram of the experimental setup. Idler radiation emerges approximately normal to the corner face of the LiNbO3 crystal and is monitored by Golay detector-light pipe combination. L is a 50-cm focal length lens, BS denotes beam splitters, PD1 and PD2 are photodiodes, and D indicates diffusers used to uniformly illuminate spectrometer slits. Pump, signal, and idler propagation directions and angles are indicated by the phase-matching triangle at upper left. Rotation of laser bench varies θ', and hence θ.