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Diagnostics and Microelectronics

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March, 1993

Lawrence
Livermore
National
Laboratory

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Diagnostics and Microelectronics

Joseph W. Balch

MASTER

1. What is the purpose of the study?

Diagnostics and Microelectronics

The Diagnostics and Microelectronics thrust area conducts activities in semiconductor devices and semiconductor fabrication technology for programs at Lawrence Livermore National Laboratory. Our multidisciplinary engineering and scientific staff use modern computational tools and semiconductor microfabrication equipment to develop high-performance devices. Our work concentrates on three broad technologies of semiconductor microdevices: (1) silicon and III-V semiconductor microelectronics, (2) lithium niobate-based and III-V semiconductor-based photonics, and (3) silicon-based micromachining for application to microstructures and microinstruments.

In FY-92, we worked on projects in seven areas, described in the reports that follow: (1) novel photonic detectors; (2) a wideband phase modulator; (3) an optoelectronic terahertz beam system; (4) the fabrication of mi-

croelectrode electrochemical sensors; (5) diamond heatsinks; (6) advanced micromachining technologies; and (7) electrophoresis using silicon microchannels.

In FY-92 construction of the new Micro-Technology Center was completed. This new state-of-the-art facility includes 7,500 sq. ft. of Class 10-1000 cleanrooms and three large dry laboratories. The building was specifically constructed for the Laboratory to exceed all federal and state safety codes and regulations. All toxic gases are stored in auto-purge gas cabinets located in separate earthquake resistant vault. All air handling machinery is mounted on a separate foundation vibrationally isolated from the cleanroom laboratories. The dry laboratories are used for microscopic inspection, packaging, and electrical and optical testing of devices. While the Micro-Technology Center is primarily a solid state device research facility, the emphasis of the thrust area is to solve problems for internal and external customers relating to diagnostic and monitoring instrumentation in a variety of scientific investigations.

Joseph W. Balch
Thrust Area Leader

B153: Micro-Technology Center

Section 3

3. Diagnostics and Microelectronics

Overview

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Novel Photonic Detectors

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This project had two parts for FY-92: (1) to fabricate a photocathode that could respond to infrared (IR) light; and (2) to fabricate a diode laser that would function as an x ray-to-light converter.

Although IR-sensitive photocathodes are not available commercially, there are numerous Lawrence Livermore National Laboratory and Department of Defense applications for such devices, including a 1.3- μm streak camera and radiation-hard IR sensors. The key part of our work on an IR-sensitive photocathode is the use of molecular beam epitaxy (MBE) to grow high quality semiconductor layers that can absorb IR light and transport the resulting charge carriers to the opposite surfaces of this electrical device. During this last year, as part of a separate research project, we discovered a new kind of photocathode and, thus, we centered our activities for both projects on fabricating and testing devices that incorporated it.

Little data had been published on the direct effects of x rays on diode lasers, and our idea was to use the absorption of x rays within the gain medium itself to modulate the optical output from a diode laser. The advantage of this device was expected to be that it should have picosecond response times since, at least in a simple double-heterostructure laser, there would be no time delay due to carrier transport. To test the device experimentally, we used a pulsed x ray source, which was a plasma that was created by a pulsed laser focused onto a metal surface. Although we did observe the direct conversion of x rays to optical output on a fiber optic, we were unable to make an accurate determination of the ultimate time response of the device.

Introduction

Photocathode

Of all materials tested, p-type GaAs, coated with cesium and a form of cesium oxide (hereafter we shall simply refer to this as 'activated'), has shown the highest quantum yield, η , for detection of visible and near-infrared (IR) light; state-of-the-art commercial GaAs photocathodes can have $\eta = 10\%$ for wavelengths out to 0.9 μm . For light with longer wavelengths, however, the GaAs is essentially a transparent material, and its use for

direct detection of IR light is not practical. While all-solid-state detectors with high values of η exist for light wavelengths longer than 0.9 μm , photocathodes offer greater radiation hardness and are well-suited to photon counting and two-dimensional imaging when used in conjunction with electron multipliers, such as microchannel plates. A radiation-hard detector with sensitivity to 1.06- μm light is desirable for LIDAR applications; atmospheric viewing can be achieved in the 1.3- to 1.8- μm band; and a photocathode with sensitivity to 1.3- μm light would find application in a streak camera that could be used for remote monitoring of physics experiments.

Figure 1. Schematic drawing of the band structure of an IR photocathode. The smaller bandgap region absorbs the IR light, to which the substrate is transparent. Light absorption promotes an electron from the lower energy level (the valence band) to the upper level, the conduction band. Since the conduction band of the layers on either side of the IR absorber is higher than that of the IR absorber, this unbiased device cannot transport the electron out of the IR absorber.

Photocathodes of $\text{Ga}_{1-x}\text{In}_x\text{As}$ or $\text{GaAs}_{1-x}\text{Sb}_x$ (for small values of x) have smaller bandgaps than GaAs and can absorb longer-wavelength light and have been fabricated elsewhere, but their values of η fall very quickly as a function of x . These photocathodes, in which a single material functions as both the IR

absorber and the electron emitter, have not shown useful single-shot sensitivity to light with wavelengths beyond $1.1\ \mu\text{m}$.

A more advanced concept, originally demonstrated by Varian EOSD, was to use a two-part semiconductor photocathode, with one part as the IR absorber (GaInAsP) and the other part as the electron emitter (InP). This two-part approach has been what we have pursued. Our idealized IR photocathode would, therefore, contain a material that could absorb the infrared light, create electron-hole pairs, and (under applied electrical bias) separate and move the electrons without loss to an activated surface for emission. This is shown schematically in Fig. 1.

We started investigating strained-layer $\text{In}_x\text{Ga}_{1-x}\text{As}$ on GaAs substrates with $\text{In}_x(\text{Al}_w\text{Ga}_{1-w})_{1-x}\text{As}$ as an emitter, but because this combination was intrinsically limited in its long-wavelength response to about $1.3\ \mu\text{m}$ and because we had recently invented a new photocathode (GaAlSb), we concentrated on this latter system, which we are in the process of patenting.

X ray-to-Light Converter

In the research area of x-ray diagnostics, one desirable feature of a detector is to encode the temporal information about the intensities directly onto a coherent optical beam, which is transmitted on an optical fiber for remote recording. One approach, originally proposed by J. Koo,¹ had been to combine a solid-state photoconductor with a diode laser, where the electrical carriers generated in the photoconductor would be used to modulate the output of the laser; this was successfully tested.² A limit to the high-speed response of such a detector is the time it takes to move electrical carriers into the gain region of the diode laser.

We proposed using the excess carriers, which are generated by the absorption of x rays in the gain region itself, as the source of modulated laser output. This has the advantage, at least for a simple double-heterostructure laser, that no time is lost for carrier transport. Since the time for the 'hot' x ray-generated carriers to thermalize has been calculated to be less than one picosecond, the overall time response for such a device should be limited only by the stimulated emission lifetime of the carriers, which can easily be a few tens of picoseconds or less. The difficulty in designing and fabricating such a device is that the x rays must pass through the top cladding layer of the laser before they can be absorbed in the gain region to create useful electron-hole pairs to modulate the optical output (Fig. 2). If the x rays have little absorption in the cladding, they will also have little absorption in the gain medium. Similarly, if they are intensely absorbed in the gain medium, they will be intensely absorbed in

Figure 2. Simple representation of the physical structure of the x ray-to-light converter. (a) Schematic drawing of the layers in the device and calculations of absorption of 1.8-keV x rays. (b) Sketch of device.

the cladding and will not reach the gain medium. Penetration depths of x rays vary rapidly with x-ray energy, so we expected our devices to be sensitive to only a rather narrow energy range of x rays in the low keV energy range. This is a range commonly produced by focused-laser plasmas.

Progress

Photocathode

During FY-92, we used our molecular beam epitaxy (MBE) system to grow heteroepitaxial structures with $\text{In}_x(\text{Al}_w\text{Ga}_{1-w})_{1-x}\text{As}$ emitters and $\text{In}_y\text{Ga}_{1-y}\text{As}$ absorber, including strained-layer superlattice buffers between the GaAs substrate and the IR absorber with electron emitter. Because activation and testing of photocathodes is a slow process, we began concentrating our efforts on $\text{Ga}_x\text{Al}_{1-x}\text{Sb}$ ($x \approx 0.3$) emitters as soon as we discovered that it worked about as well as GaAs (Fig. 3). The main appeal of the $\text{Ga}_x\text{Al}_{1-x}\text{Sb}$ emitter is that it is lattice-matched to single-crystal IR absorbers, which span the range of wavelengths from 0.9 μm to more than 10 μm . GaSb absorbs out to 1.7 μm , InAs reaches 4 μm , and InAs/ $\text{Ga}_w\text{In}_y\text{Al}_{1-y-w}\text{Sb}$ superlattices have been shown to absorb out to 12 μm . We have grown, activated, and tested numerous photocathodes of $\text{Ga}_x\text{Al}_{1-x}\text{Sb}$, and we have grown superlattices of InAs/GaSb, which we expect to absorb in the 0.9- to 2- μm range. We are still investigating doping levels in the various layers to minimize dark currents. Dark currents degrade the performance of these devices.

X ray-to-Light Converter

To fabricate an appropriate device, we used our MBE to grow a simple DH laser with 70% aluminum in the cladding. This high aluminum content increased the overlap of the optical beam with the carriers in the gain region and also allowed more x rays to pass through the cladding and enter the gain region for absorption. Because our simple modeling showed that our devices, with 0.7- μm thick cladding and 0.3- μm thick gain region, would exhibit peak sensitivity for x rays with energies of a few keV, we had to discontinue using our normal top-side metallization of titanium/platinum/gold and substitute pure aluminum. (The gold and platinum would have absorbed virtually all of the desired x rays.) This required our developing a new metallization procedure and a wire bonding procedure for the aluminum contact.

We also designed and built a heat sink to mount this device, and the heat sink had to be designed so that the epoxy that we used for F-O pigtailling would not flow onto the laser facet, yet would allow accurate

Figure 3. Plots of photoresponse for a variety of GaAs and GaAlSb photocathodes that were grown on our MBE and activated in our test apparatus.

placement of the FO proximal to the emitting facet. We then mounted the assembled laser on a vacuum flange with a fiber-optic connection through the flange. Using x rays from a focused-laser plasma, we did observe the direct conversion of x rays to coherent optical light, as hoped (Fig. 4). Because the laser pulses were multi-nanosecond in duration, we could not determine the shortest time response of our detector. However, we did learn that the pulse-to-pulse variations in x rays that were generated by the focused laser caused far more variation in the output of our detector than in the simple photoconductive detectors. This, again, is due to the fact that our absorbing region is 0.8 μm beneath the surface of the laser (0.7- μm -thick cladding with 0.1- μm -thick electrical contact layer).

The data shown in Fig. 4 represent the average of 100 laser pulses. When we tried the same experiment with a subpicosecond x ray source with less total fluence, we were not able to detect x rays.

Future Work

We are patenting the new $\text{Ga}_x\text{Al}_{1-x}\text{Sb}$ /IR-absorber photocathode. An Engineering Research

Figure 4. Plot of laser output vs time for our x ray-to-light converter, averaged over 100 laser pulses.

Division project at Lawrence Livermore National Laboratory is working on its development and seeking an industrial partner. The x ray-to-light converter is not currently being pursued further.

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Wideband Phase Modulator

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Lithium niobate integrated optics work has been an ongoing effort at Lawrence Livermore National Laboratory (LLNL) for many years. We have delivered completely packaged Mach-Zehnder modulators with bandwidths to 20 GHz, extinction ratios over 40 dB, and losses as low as 4 dB, to LLNL programs. These devices have traditionally been used to intensity-modulate laser sources in high-speed analog links. During the past year, we have been doing research on a very broad bandwidth, integrated-optic phase modulator. Such a device would have immediate applications to stimulated Brillouin scattering suppression in both optical fibers and glass amplifiers. In addition, these devices can be used to generate very short optical pulses from long or even cw laser pulses (pulse compression). Although neither of these applications is new, what is unique here is the efficient, integrated-optical phase modulator used to implement these techniques.

Introduction

Pulse Compression

Current commercial capability in generating picosecond optical pulses usually involves large, expensive table-top laser systems, which greatly restricts the applications of these systems. A picosecond, compact, inexpensive pulse compressor suitable even with cw laser sources can be built with an ultra-high bandwidth, LiNbO_3 phase modulator together with a dispersive element such as a grating or a fiber. In fact, these optical pulse generators can be built at any wavelength where suitable optical waveguides can be built. Previous attempts to compress and generate picosecond pulse trains using phase modulators used bulk devices and, hence, required many kW of microwave power to achieve picosecond pulses and optical bandwidths of 600 GHz.¹ One other author has tried a guided-wave device. However, a low drive power and an inefficient electrode structure limited the bandwidth to 12 GHz.²

The bandwidth of a phase modulator is directly proportional to the drive voltage and inversely proportional to V_π , which is the voltage required to produce a phase change of 180° in the optical carrier. By using integrated optics as opposed to

bulk optics, V_π can be reduced to 10 volts or less. Higher electrode voltages can be achieved for a given drive voltage by using resonant electrodes. We have been working to achieve a Q-factor on the order of 100 in a microwave transmission line resonator designed in an integrated fashion with the optical waveguide. At resonance, the voltage applied to the electrodes is approximately the source voltage multiplied by the square root of the Q-factor. We estimate that bandwidths on the order of 500 GHz can be achieved with microwave power levels on the order of several watts. Using a dispersive element, this bandwidth can give rise to picosecond pulses from optical sources. For a transform limited pulse, the minimum pulse width obtainable is given by $.8/(\text{bandwidth})$. Therefore, for 500 GHz of bandwidth, 1.6 ps pulses can be obtained. **Figure 1** shows the concept for pulse compression.

Stimulated Brillouin Scattering Suppression

Stimulated Brillouin scattering (SBS) is a nonlinear optical effect that limits the maximum optical power that can be transmitted in both glass amplifiers and glass fibers. For example, at 800 nm, experimental evidence exists that shows optical power

Figure 1. Optical pulse compression with a wideband phase modulator to chirp the incoming laser.

saturation at about 100 mW in fiber. The SBS is inversely proportional to optical linewidth. Therefore, it is more difficult to obtain power transmission with a narrow linewidth laser. To suppress the negative effects of SBS, the linewidth can be widened with phase modulation. Experiments are planned to see how the wideband phase modulator can be used to minimize the SBS problem.

Progress

The goal of FY 92 work has been to design and fabricate a high Q electrode structure. We have

gone through three iterations of electrode design this year. To maximize the overlap of the optical and electrical waves, the microwave electric field must be confined to a gap of about 10 μm . A tight gap electrode structure can be limited in Q since the microwave current bunches in the conductors close to the gap. We have both modeled and built microwave resonant electrodes from symmetric coplanar and asymmetric coplanar lines. We have studied shorted and open-ended lines. In addition, we have studied how the microwave energy is coupled to the resonant electrode.

In our first iteration, two electrode structures were packaged in one box for test purposes. We discovered that the microwave energy excited not only the electrode of interest, but the additional electrode in the same box. The first iteration used both an asymmetric line and an asymmetric input-coupling scheme. In our second iteration, symmetric lines were used for both the input coupling line and the resonator. These devices were tested with high frequency rf probes and a network analyzer. Network analyzer measurements of these structures indicated two poorly defined resonances. Further computer modeling with a commercial electromagnetics program (Sonnet EM) indicated that resonances were achieved at slightly different frequencies for waves on either side of the resonant electrode. This was probably due to the perturbation of symmetry from the center feed point on one side of the electrode.

Another electrode pattern that was identical except that it had a 100- μm gap, did not have this problem. However, the wide gap is incompatible with building a high efficiency modulator. The third iteration produced a well defined notch in the reflection coefficient. This indicated that the electrode was indeed resonant and that a substantial amount of input power was coupled to it.

Figure 2. Plots of (a) calculated and (b) measured reflection coefficient, S11.

Figure 3. Current distribution on electrode at resonance.

In this electrode design, the input coupling consisted of a symmetric coplanar line, and the resonant electrode was an asymmetric coplanar line. This alleviated the problem that existed in the completely symmetric resonator.

Figure 2 shows both the calculated and measured reflection coefficient, S_{11} . The resonance has a Q of about 25, which corresponds to a 5-times voltage enhancement. The depth of the notch is no greater than 5 dB, indicating that about one-third of the incident power is not coupled into the resonant electrode. A new mask with a wider coupling gap has improved this notch depth to about 10 dB or 90% coupling. The slight differences in notch depth and resonant frequency between the modeled and measured data can probably be accounted for by the fact the modeling code is two-dimensional and does not take into account the effect of electrode thickness.

Figure 3 shows a current distribution picture at resonance, with most microwave current crowded near the tight 10- μm gap.

Future Work

Currently, the modified asymmetric electrode structure shown in **Fig. 3** is being electroplated on top of an 800-nm optical waveguide. Once fabricated, the devices will have their bandwidths evaluated with an optical spectrometer. If sufficient bandwidth, in the neighborhood of 500 GHz, is achieved, the chirped pulses will be compressed with a grating to achieve picosecond optical pulses. In related integrated-optics work, we are exploring the use of modulators at superconducting temperatures. We would like to explore the possibility of building one of the resonant electrode phase modulators with niobium electrodes to determine what type of Q can be achieved at superconducting temperatures.

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Optoelectronic Terahertz Beam System: Enabling Technologies

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In FY-92, we investigated the photoelectronic properties of semiconductor materials and structures for implementation as photoconductive dipole antennas in a terahertz beam system. We have measured optically generated electrical pulses propagating on-chip having temporal resolution as short as 1 ps. Furthermore, our devices have been used in a terahertz beam system to generate and detect electromagnetic pulses traveling through free space, with durations as short as 500 fs.

Introduction

With the advent of sub-picosecond laser sources, optoelectronic switching devices can be used to emit broadband electromagnetic (EM) pulses into free space. Integrated metal-semiconductor-metal photoconductive devices are capable of radiating EM pulses from monolithically integrated antenna structures.^{1,2} The basic system concept is illustrated in Fig. 1. A static electric field is stored across the electrodes of the highly resistive, photoconducting antenna structure. When an optical pulse of intensity E_{opt} is incident between the electrodes, the conductance of the photoconductor increases, and the relation between the radiated electric field and the static electric field strength is described by³

$$E_r = -E_s \sigma_s \eta_0 / [\sigma_s \eta_0 + (1 + \sqrt{\epsilon})], \quad (1)$$

where ϵ is the dielectric constant of the antenna material, η_0 is the free space impedance, E_s is the static electric field applied across the photoconductor, and σ_s is the conductivity of the photoconductor due to the photogenerated carriers. The conductivity is described by

$$\sigma_s = q \mu_{eff} (1 - r) E_{opt} / h\nu, \quad (2)$$

where q is the electronic charge, r is the reflectivity, μ_{eff} is the effective mobility, $h\nu$ is the photon energy, and E_{opt} is the optical energy density. From Eqs. 1 and 2, it can be seen that the effective mobility of the photoconductor material directly relates to the efficiency of the radiating

antenna element. Therefore, this research will focus on optimizing the mobility of materials used as photoconducting antenna structures, which are suitable for compact arrays of emitters for ultra-wideband radar and remote applications. The advantages of using integrated optoelectronic antenna structures include ultra-wide bandwidth, high power, excellent directionality, low cost, and compact, durable elements conducive to large, photonically controlled arrays.

Progress

The power radiated by the photoconductive antenna element is directly related to the electronic transport properties of the semiconductor material being used. In particular, a semiconductor material that retains high mobility for the

Figure 1. Schematic diagram of photoconducting antenna emitter and detector.

Figure 2. Autocorrelation circuit configuration.

Figure 3. Impulse response of LT-GaAs photoconductor measured by reflective electro-optic sampling.

Figure 4. (a) Waveform and (b) corresponding Fourier Transform of radiated pulse detected with LT-GaAs detector in terahertz beam system.

photogenerated carriers while providing fast recombination lifetimes is desirable. In general, these two electronic properties conflict. Recently, it has been found that the growth of GaAs by molecular beam epitaxy (MBE) at low substrate tempera-

tures (190° to 400° C) introduces large concentrations of point defects to the crystal structure through the incorporation of excess arsenic into the lattice.⁴ During thermal annealing of the epitaxial layer at temperatures ranging from 580° to 800° C, the excess arsenic diffuses to form precipitates. Depending on the anneal time and temperature, the resulting arsenic precipitates have diameters ranging from 2 to 20 nm and spacings ranging from 5 to 50 nm. It is believed that these defects are metallic in nature,⁵ behaving as fast recombination centers and resulting in sub-picosecond photoconductive response times. Furthermore, since the epitaxial LT-GaAs retains excellent crystalline quality, higher mobility is exhibited, which translates to higher sensitivity in comparison to alternative materials for picosecond photoconductivity.

Photoconductive autocorrelation circuits, illustrated in Fig. 2, have been fabricated from LT-GaAs grown by MBE at 190° C. This circuit uses the 'sliding' contact configuration,⁶ which consists of two balanced coplanar lines with 5-μm width and 10-μm separation. With an electric field applied across the coplanar lines, an electrical transient signal can then be launched onto the lines by shorting the gap between them with an optical pulse. The photoconductive pulse can be generated at any point along the coplanar lines, hence 'sliding' contact. This is especially useful for characterizing the dispersive effects of the coplanar lines. To measure the transient electrical pulse, a sampling element is positioned along one of the lines in the coplanar pair (Fig. 2). The sampling can be either photoconductive⁷ or electro-optic.⁸ By varying the relative delay between the generating and sampling optical pulses, the photoconductive transient response is measured. Figure 3 illustrates the electrical pulse measured for this material, by the reflective electro-optic sampling technique.⁹ The optical pulse width is ~ 600 fs at 820-nm wavelength, and the signal has propagated approximately 100 μm on the transmission line. The response is ~ 1 ps full width at half maximum. Calibration of the incident optical intensity gives an estimated mobility for this material of ~ 120 cm²/Vs, which is a factor of 4 to 10 times larger than that of other materials used for picosecond photoconductivity.⁷

Initial measurements of our devices in a terahertz beam system have been conducted by researchers at Columbia University.¹⁰ Results from these experiments have demonstrated that our devices are capable of detecting transient electric fields having amplitudes in excess of 1 kV/cm with temporal resolution of 600 fs. The measured

response is illustrated in **Fig. 4a**, the corresponding frequency domain response in **Fig. 4b**. From these results, it can be seen that these pulses have useful frequency content beyond 1 THz. This renders terahertz beam systems useful for further applications such as far-infrared spectroscopy, imaging, and ultra-wideband communications.

Future Work

This research has demonstrated the suitability of our devices as high-performance, photoconducting antenna elements. The next step is to implement photonically controlled phased arrays based on this technology. This will be done by implementing integrated optics technology as the active system component to embed the rf signal, and phase modulation on the optical carrier to achieve beam-steering functionality. The combination of these technologies will make this system extremely useful for airborne and space-based applications.

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Fabrication of Microelectrode Electrochemical Sensors

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We are using integrated circuit technology to fabricate microelectrode electrochemical sensors. These sensors have improved performance compared to those that use a single macroelectrode. The near-term application for these new sensors is for environmental monitoring, especially for heavy metal contamination.

Introduction

An electrochemical sensor consists of a pair of dissimilar electrodes immersed in a solution containing unknown ions, as shown in Fig. 1. The relationship between the current in the working electrode (I_w) and applied potential (V_w) referenced to a reference electrode, depends on the ions in solution and on the composition of the electrodes. This sensor is particularly well suited for the measurement of heavy metal contamination and pH as needed in environmental monitoring.^{1,2} The goal of this project was to use integrated circuit (IC) microfabrication technology to fabricate multielectrode electrochemical sensors.³ The advantages of using microelectrodes in electrochemical sensors are: (1) immunity from uncompensated resistance effects because of low currents used; (2) high rates of mass transfer and hence higher sensitivity; (3) higher signal-to-noise ratios; (4) the potential for extremely fast experiments; and (5) the extension of normal electrochemical background limits.

In addition, the use of a matrix of different electrode materials improves the information content of the measurement. Also, because of the mass-production capability of microfabrication, reproducible sensors can be produced inexpensively and used in a disposable fashion.

Progress

This past year, we used the photolithography and vacuum evaporation capabilities available in the MicroTechnology Center of Lawrence Livermore National Laboratory to fabricate microelectrode electrochemical sensors. Figure 2 shows a computer drawing of the sensor electrodes. In one design, silver was used for the reference electrode, platinum for the counter electrode, and the four working electrodes were platinum, platinum, iridium oxide, and silver. In one application, the iridium-oxide working electrode is used as a pH sensor: one of the platinum working electrodes is coated with a mercury thin film

Figure 1. Typical electrochemical sensor arrangement. The relationship between the current I_w and the applied potential V_w depends on the electrode materials and the ions in solution.

Figure 2. Electrode configuration of the microelectrode electrochemical sensor.

to detect lead, cadmium, zinc, and copper ions; the other platinum working electrode is coated with a polymer to detect heavy metals; and the silver working electrode is used to detect chlorine.

We devoted considerable effort to the development of a reliable fabrication process. Silicon wafers, 1-mm-thick, were used as substrates so that conventional IC processing equipment could be used. The thickness was chosen so that they would be robust enough to allow handling without breakage, and so that commercial connectors could be used to interface the sensors with the processing electronics. A combination of 5000 Å of thermal oxide plus 2000 Å of silicon nitride was used to electrically isolate the sensor films from the silicon substrate. Two sensors were fabricated on each wafer, and we could process six wafers at a time in the vacuum system. When completed, the sensors were cut with a dicing saw to their final size of 0.5 in. × 1.5 in.

Figure 3. Photograph of two completed microelectrode electrochemical sensors. The pads at the top interface to a commercial connector.

Since the materials used for this sensor fabrication were not those that one typically finds in IC processing, we had to deal with new problems of film adhesion, cracking, and compatibility. Originally, we tried an etch procedure to define the sensor material, but this was difficult because of the incompatibility of the resist with some of the etches. In addition, it was difficult to completely etch away the films, and this caused some conductivity between the various electrodes. We eventually settled on an all-lift-off procedure for the sensor fabrication. With this approach, openings are patterned in the photoresist layer, the sensor material is then evaporated onto the entire wafer, and the unwanted material is lifted off by dissolving the resist in acetone. This eliminated the need for any chemical etching. After the sensor materials were defined in this manner, a photosensitive layer of polyimide was applied to the wafer and patterned with the openings required for the sensor electrodes and the connector pad area. The typical circular area of the exposed working electrode had a diameter of 50 μm. **Figure 3** is a photograph of two completed sensors.

Following fabrication, the sensors were interfaced to a data collection system, and experiments were performed. In many cases, a 'textbook' response was obtained from the sensors for the ions of interest.

Future Work

Future work will involve experiments with electrodes having different sizes and shapes, to try to optimize the performance of the sensor. We will also work with other sensor materials that are more specific to the ions of interest. The fabrication process will be refined to improve the overall yield of useful sensors. We will also modify the vacuum evaporator so that we can simultaneously fabricate 24 instead of 12 sensors. Finally, we will start working with an industrial partner, since some early versions of this sensor appear ready for commercialization.

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Diamond Heatsinks

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We are studying patterned diamond films for use as heatsinks to cool solid-state laser diodes. We have etched diamond slabs using our chemically assisted ion beam etcher. An inductively coupled plasma torch has been set up for the high rate deposition ($> 50 \mu/h$) of diamond films onto patterned silicon wafers. Our modeling effort was used to design the optimum dimensions for both types of heatsinks.

Introduction

For some time, Lawrence Livermore National Laboratory has been using silicon microchannel heatsinks to cool solid-state laser diodes. Very intricate microchannels have been etched into the surface of silicon wafers to provide paths for cooling water. The packaging has been designed so that diode bars can be stacked together to maximize the radiated flux.¹ In some designs, a heat dissipation approaching 3000 W/cm^2 has been achieved.

To expand our heatsink options, we have been studying the use of patterned diamond as a heat-sink material. Diamond makes an excellent heat-sink because it has the highest thermal conductivity of any known material at room temperature, i.e., $20 \text{ W/cm}^\circ\text{C}$ vs $1.5 \text{ W/cm}^\circ\text{C}$ for silicon. It is also an excellent electrical insulator ($1 \times 10^{16} \Omega\text{-cm}$) and will not corrode. Until recently, diamond had not been used extensively for heatsinks because of its high cost. However, recent advances in the deposition of diamond films using chemical vapor deposition (CVD) techniques has lowered its cost. These CVD films are now commercially available from several vendors and are being used as heatsinks. The thermal conductivity of CVD diamond is somewhat lower than that of natural diamond, i.e., $14 \text{ W/cm}^\circ\text{C}$ vs $20 \text{ W/cm}^\circ\text{C}$, but it is still high enough to make the material very attractive. All of the commercially available diamond is in the form of flat slabs. Our emphasis is on patterned diamond slabs. The patterning can be used for water flow channels or for slots into which laser diode bars are inserted.

Progress

During FY-92, we worked on three aspects of the diamond heatsinks problem: modeling, etching, and film deposition. The modeling effort consisted of refining a code, originally developed by Landram,² to make it more user friendly and more efficient for analyzing silicon and diamond. **Figure 1** shows the heatsink configuration used in the modeling work. In this Figure, a heat generating device is shown bonded to a microchannel heat-sink. There are five thermal impedances in this structure that limit heat flow: (1) μ_{spread} (μ_{sp}), the spread of heat from a point source generator; (2) μ_{bulk} (μ_{bu}), the flow of heat through the bulk of the heat generating device; (3) $\mu_{\text{interface}}$ (μ_{in}), the flow of heat across the eutectic bonding material; (4) $\mu_{\text{convection}}$ (μ_{conv}), the flow of heat from the eutectic bonding material to the cooling fluid; and

Figure 1. Cross section of a solid-state device bonded to a microchannel heat-sink.

Figure 2. Cross section of a microchannel heatsink illustrating the design parameters.

(5) μ_{conv} (μ_{af}), the removal of heat by the cooling fluid. Our modeling effort concentrated on μ_{conv} , which concerns the optimum design for the microchannels. We were able to compare microchannels fabricated from silicon and diamond.

Figure 2 is a cross section of a microchannel heatsink illustrating the parameters used in the modeling. The model calculates the thermal impedance for the microchannel heatsink, μ_{conv} . Knowing μ_{conv} , we can immediately determine the difference between the average temperature of the cooling fluid and the temperature of the fin-base, as identified in **Fig. 2**. This temperature difference is given by $\Delta T = (\mu_{\text{conv}})(q)$, where q is the heat flux applied to the heatsink in W/cm^2 . Thus, a low value for μ_{conv} is desired, and the optimum values for the dimensions of the microchannels are determined by those that give the lowest μ_{conv} .

Figures 3a and **3b** are three-dimensional plots of the thermal impedance for silicon and diamond microchannel heatsinks. Both are for a channel width (W_c) of $20\text{ }\mu\text{m}$. For silicon heatsinks with a wall thickness (W_w) of $20\text{ }\mu\text{m}$, the optimum channel height (H) is $\sim 180\text{ }\mu\text{m}$. Beyond this, not much is gained. For diamond, also with a W_c of $20\text{ }\mu\text{m}$ and a

W_w of $20\text{ }\mu\text{m}$, H is $\sim 700\text{ }\mu\text{m}$. If these values could be achieved, the diamond heatsink would outperform the silicon heatsinks by a factor of four. This height, however, is rather impractical from a fabrication point of view, but our modeling has shown that if diamond heatsinks were fabricated with the same wall height as silicon, the thermal impedance would be lowered by a factor of two.

To create flow channels in diamond, we performed a number of etching experiments using our chemically assisted ion beam etcher (CAIBE). The diamond was purchased from two different vendors. One vendor supplied free-standing slabs that were $5 \times 5\text{ mm}$ and 0.3-mm thick. The diamond was deposited by CVD. The other vendor supplied diamond bonded to a 1.5-mm -thick tungsten carbide substrate. This film was $600\text{-}\mu\text{m}$ thick, and the diameter of the part was 26 mm . It was deposited by a hot pressed technique and then polished smooth. We deposited a $1000\text{-}\text{\AA}$ -thick chromium film on both types of parts, patterned the chromium using photolithography and a wet chemical etch, and then etched the diamond in our CAIBE. The etching experiments followed work by Geiss.³ In this experiment, the diamond is bombarded with xenon ions that have been accelerated to an energy of 700 eV . At the same time, the sample is flooded with a source of oxygen, such as N_2O or NO_2 gas. The bombarding xenon ions promote chemical etching and, since they are collimated and directional, the etching proceeds in a directional manner. Under these conditions, an etch rate of approximately $200\text{ }\text{\AA}/\text{min}$ is achieved. When the xenon ion energy was increased to 1800 eV , the etch rate doubled to $400\text{ }\text{\AA}/\text{min}$. Unfortunately, the chromium mask also erodes away, limiting how deep one can etch. With a $1000\text{ }\text{\AA}$ -

Figures 3a and 3b. Three-dimensional plots of the thermal impedance of (a) silicon and (b) diamond microchannel heatsinks. The channel width is $20\text{ }\mu\text{m}$ in both cases.

thick chromium mask, we could only etch to a depth of $0.5\text{ }\mu\text{m}$. We are looking at other mask materials such as oxides that may be more durable to the ion beam.

We also studied the deposition of diamond films onto patterned silicon substrates. The plan was to deposit thick diamond onto a silicon substrate that already had deep flow channels etched into its surface. The silicon could then be etched away, leaving a patterned diamond film. **Figure 4** shows cross sections of the silicon wafers prepared for the deposition. The etched grooves are all $20\text{-}\mu$ wide, on $40\text{-}\mu$ centers. The depth-to-width ratios used were $20/20$, $40/20$, $100/20$, and $200/20$. In May of 1992, we gained access to an inductively coupled plasma (ICP) torch to be used for the diamond film deposition. This equipment has been used by others to deposit diamond films at rates as high as $50\text{ }\mu/\text{h}$.⁴ The high-velocity directional flow of the gases should make this technique ideal for the deposition of diamond into preformed grooves. **Figure 5** shows a diagram of this machine. It uses argon, hydrogen, and methane as source gases and is powered by a 50-kW , 4-MHz generator. From May to October of FY-92, we worked on the gas control system, and built cooling chambers and wafer holders. A number of calibration runs were made to adjust the plasma operating conditions. Actual film depositions are planned for early FY-93.

Figure 4. Scanning electron microscope cross sections of silicon wafers to be coated with thick diamond films.

Future Work

Our modeling effort needs to be extended to include the other four thermal impedances discussed above. This will help designers optimize the complete diode package instead of only the

Figure 5. Diagram of the ICP torch used for high-rate diamond film deposition.

heatsink itself. Experiments need to be conducted with other mask materials in our CAIBE to find those with low etch rates so that we can etch deeper structures. Finally, and most important, we need to use the ICP torch to deposit thick diamond films into silicon grooves and then etch away the silicon. If successful, this will be the first report of a diamond slab with deep vertical channels.

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Advanced Micromachining Technologies

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We have developed several innovative micromachining techniques that will facilitate the future development of high-tech microtechnologies, such as microelectronics, microstructures, microactuators, microsensors, and microinstruments. The Corner-Protection Technique will produce sharp convex corners and clear scribe lines in any anisotropic etching process. The Circular Etching Process alone, or combined with Selective Wet Chemical Etching for Boron Nitride Film, can be used to fabricate numerous forms of new, round features that were previously unattainable.

Introduction

Over the last two decades, single-crystal silicon has been increasingly used in a variety of new applications besides microelectronics. Single-crystal silicon is not just a good semiconductor material; it is also an excellent mechanical material for microscale devices, such as microstructures, microactuators, microsensors, and microinstruments. To facilitate the development of these new high-tech devices, newer and better micromachining technologies have to be created for the fundamental fabrication processes.

Recently, we have developed several new micromachining processes. These new processes will allow us to make microscale features that were previously unattainable. The Corner-Protection Technique will allow us to make precise sharp-corner features, without rounding the corner by undercutting. The Circular Etching Process, which uses isotropic etching with boron nitride as the masking film, is well engineered to fabricate circular thin film membrane windows or circular microstructures. Combined with Selective Wet Chemical Etching for Boron Nitride Film, this Circular Etching Process can build clear circular microstructures with or without additional films.

Progress

Corner-Protection Technique

Microscale features on silicon wafers are very often achieved by means of anisotropic wet chemical etching. However, most of these etching pro-

Figure 1. Comparison of the Lawrence Livermore National Laboratory (LLNL) Corner-Protection Technique and the regular etching technique on the anisotropic etching of a (110) silicon wafer: (a-I) the clear 109.4° corner etched by the LLNL technique; (a-II) the sharp 70.6° corner etched by the LLNL technique; (b-I) the undercut 109.4° corner etched by the regular technique; and (b-II) the undercut 70.6° corner etched by the regular technique.

Figure 2. An example of the round features etched by the Circular Etching Process.

cesses have a severe undercutting problem at any convex or outer corner of a chip or device feature. This undercutting problem will limit the compactness and effectiveness in the overall design.

We have successfully developed a novel method for protecting these convex corners with very little space. This technique can produce sharp convex corners and clear scribe lines at any desirable etching depth. It can make many previously impossible geometries possible.

Last year, we demonstrated the technique on (100) silicon wafers to make narrow-frame thin film membrane windows, also known as "thin-wall windows." This year, we extended the technique to (110) silicon wafers. **Figure 1** compares results with and without the Corner-Protection Technique. This successful demonstration has provided a possible licensing opportunity with Endevco, a designer and manufacturer of instrumentation for vibration, shock, and pressure measurement.

Circular Etching Process

Most micromechanical devices rely on traditional anisotropic KOH etching for fabricating the microfeatures. This etching technique will produce only features with straight boundaries. Since it is desirable to have round features in many applications, we have put a great deal of effort into the development of special circular etching techniques to create new and unique microstructures.

First, we carefully engineered an isotropic etching process with $\text{HCl} + \text{HNO}_3 + \text{CH}_3\text{COOH}$ to produce even etching in all directions. Boron nitride thin film was used as the etching mask because of its chemical compatibility with the etchant. Circular boron-nitride

Figure 3. Comparison of the boron nitride-coated, round silicon disks etched by LLNL Selective Wet Chemical Etching and Dry Plasma Etching: (a) the shiny, small, round silicon disk after Selective Wet Chemical Etching; and (b) the foggy, small, round silicon disk after dry plasma etching.

thin film windows and other round microstructures were fabricated in this way (**Fig. 2**).

For this circular etching technique to be more useful as a tool when making round features for general applications, it is sometimes desirable to remove the masking boron nitride thin film. Conventionally, the boron nitride film can be removed only by dry plasma etching. However, plasma etching is not very selective—it also etches silicon nitride film, silicon-based substrate or film, and even gold film.

Our contribution to the solution of this problem is the development of the first wet chemical process that will selectively etch only boron nitride, but not coatings or substrates of silicon, silicon nitride, and silicon dioxide. The etchant is a very strong oxidizing reagent of sulfuric acid and hydrogen peroxide. It can remove the boron nitride film very selectively and smoothly, without leaving any over-etched surfaces, as the plasma etching process does (**Fig. 3**).

This modified round etching process was also demonstrated to be very useful in the development of the microcapillaries for the Miniaturized Gas Chromatography Project of Conrad M. Yu and the author. □

Electrophoresis Using Silicon Microchannels

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We are developing electrophoresis techniques in microchannels that can be micromachined in substrates. We have developed a model of electro-osmotic flow in free-solution capillary electrophoresis when an external electric field is applied to the walls of the capillary. Also, we have begun development of gel-filled microchannels to be used for electrophoresis of biological materials.

Introduction

Electrophoresis is the separation of charged ions or molecules in a solution based on their differential migration in an applied electric field. It is widely used in modern analytical chemistry to separate charged particles in ionic solutions, and in biochemistry to separate biomolecules. The emergence of the biotechnology industry has greatly increased the interest in various electrophoresis methods. Our objective is to develop methods for novel electrophoresis of liquid ionic solutions and charged biological material, in microchannels in silicon and other substrate materials. Silicon microchannels for electrophoresis have potential advantages over conventional quartz capillaries due to (1) enhanced thermal dissipation of heat generated during electrophoresis, because the thermal conductivity of silicon is nearly 100 times that of quartz; and (2) the construction of a high-density array of microchannels on a single substrate in silicon and other materials, using modern microfabrication technology. Silicon-based microfabrication technology also provides a promising way to incorporate field plates around an electrophoresis microchannel to control the electro-osmotic flow of solution in free-solution electrophoresis. Control of electro-osmotic flow in free solution electrophoresis is a promising means to improve separation resolution and to allow separation of solutes in relatively short capillaries (i.e., 1 to 10 cm).

Progress

Our previous efforts¹ demonstrated control of electro-osmotic solution flow in round quartz capillaries and rectangular silicon microchannels, by applying an external electric field perpendicular to the inner walls of the electrophoresis capillary or rectangular channel. The electro-osmotic flow of the solution is caused by the force of an axial electric field upon a diffuse, dipole charge sheath in the solution adjacent to the capillary wall. This sheath is created by the electrostatic attraction of charge surface states of the capillary wall on solvated ions in the electrolyte. As the mobile part of the sheath is moved along the capillary wall by the applied electric field, the solvated ions of the diffuse layer transfer momentum to the remainder of the electrolyte solution. Therefore, the whole solution moves with the diffuse layer, and plug-like flow is created in the capillary. We can control the mobility of the electro-osmotic flow by applying an external electrostatic field perpendicular to the capillary wall, so the diffuse dipole layer in the electrolyte is modulated or eliminated.

Figure 1 shows a typical experimental result we obtained previously for the electro-osmotic mobility in a quartz capillary as a function of the external voltage applied perpendicular to the capillary walls. Our experimental setup was quite similar to that of the University of Maryland, where two concentric quartz tubes each filled with elec-

Figure 1. Measured electro-osmotic mobility of an electrolyte solution (2 mM concentration) in a 50- μm internal diameter capillary as a function of voltage applied across the 167.5- μm -thick capillary wall.

trollytes were used.^{2,3} The inner tube was for the electro-osmotic flow; the outer tube was used to provide the external bias electric field. In our experiment, we continuously increased the bias voltage up to 10 kV. At about 7 kV, the electro-osmotic flow changed its direction. Here, we noticed that the rate of change of the mobility was not exactly a linear function of the externally applied voltage. However, we could fit the curve with two linear lines: one when the mobility is positive and another when the mobility is negative. This is expected because, as the direction of electro-osmotic flow changes, the moving cations are replaced with anions.

Model for External Electric Field Control of Electro-osmosis

This year, we developed a theoretical model of external electric field control of electro-osmotic flow to gain additional insight into the physical mechanisms of electro-osmosis. This model allows us to relate the functional dependence of measured electro-osmotic mobility vs the applied external voltage, to the density of surface states on the quartz wall and the ionic concentration of the electrolyte. Our model of the capacitive and interface-charging phenomena in a conductor-insulator-electrolyte capillary structure is adapted from a model widely used for similar phenomena in Metal-Insulator-Semiconductor capacitors used in microelectronics.⁴ This type of model can easily be interpreted in terms of an electrical equivalent circuit. Figure 2 shows this model's equivalent circuit for our experiment, where two concentric capillaries are each filled with electrolytes. In this equivalent circuit, the externally applied voltage is shared among a series of capacitors.

An extensive set of equations was derived that relates the various elements in the equivalent circuit to important physical quantities such as electrolyte concentration, viscosity of the electrolyte,

the thickness and dielectric constant of the quartz wall, the surface state density of the quartz wall, and the applied voltage that controls the electro-osmotic flow. From these equations, we are able to relate the change in electro-osmotic mobility as a function of applied voltage (i.e., the slope of the curves in Fig. 1) to the density of surface states on the quartz wall for a given electrolyte concentration. For experimental results such as shown in Fig. 1, our analysis shows that when the anion traps are replaced by cation traps, there is a significant change in the density of the surface state per volt, while the total surface state densities per square centimeter (Ns) under the two different conditions are nearly the same. This indicates that the total number of active surface states, Ns, on the silicon dioxide are determined by the initial chemical conditions, and the active sites are bipolar in nature. The calculated value ($2.4 \times 10^{12} \text{ cm}^{-2}$) of the

Figure 2. The electrical equivalent circuit model of two annular capillaries, each filled with electrolytes. The outer capillary is used to apply an external electric field to the walls of the inner capillary to control electro-osmosis in the inner capillary. C_{eo} represents the capacitance of the electrostatic diffuse layer between the capillary wall and the outer aqueous interface. C_c represents the capacitance of the inner capillary tube. C_{ei} represents the capacitance of the electrostatic diffuse layer between the inner capillary wall and the inner aqueous interface. R_{si} and R_{so} are surface resistances for the inner and outer surfaces, respectively. The surface capacitances C_{so} and C_{si} represent the surface state densities per volt on outer and inner surfaces of the capillary.

surface state densities is, however, much smaller than that normally accepted ($5 \times 10^{14} \text{ cm}^{-2}$). This is so because the values measured are the number of active sites, which are shown to be dependent upon not only the surface condition but also the different pH's, ionic strength, and liquid densities. From experimental data,¹ we calculated the values for Ns and found that the values of Ns under experimental conditions similar to ours were of the same order of magnitude, but increased close to one order of magnitude as the electrolyte concentration increased from 1.5 mM to 50 mM.

Electrophoresis of Biological Materials

This year, we also began an investigation of electrophoresis of biological materials in gel-filled silicon microchannels. Gel electrophoresis is widely used for separating biological materials such as DNA fragments. Almost all clinical, molecular, or forensic projects that involve the characterization of DNA are dependent upon the separation and/or purification of DNA fragments by one or more methods. By far, the most common method is based upon electrophoresis. Since the DNA double-helix backbone is negatively charged, fragments of DNA migrate toward the anode when placed in an electric field. If the DNA is caused to migrate through a sieving matrix such as agarose or polyacrylamide, fragment mobility is a function of fragment size, i.e., the smaller fragments migrate faster than larger fragments. In our experiments, we filled microchannels that had been etched in silicon substrates, with agarose gel. **Figure 3** shows the results obtained using a standard 4-mm-thick agarose gel compared to those for a thinner gel supported in a 1-mm-thick etched silicon channel. These results indicate that not only is it possible to separate the fragments in a structure of these dimensions, but more important, both the resolution and speed of the separation are enhanced. We expect that the significantly higher thermal conductivity of silicon, compared to that of standard glass materials used in conventional gel electrophoresis, will enable electric field separations to be done at much higher electric fields to achieve faster separation.

More experimentation is required to verify the expected improvement in separations by going to smaller (i.e., thinner and narrower) gels. We have performed experiments that indicate the definite

Figure 3. A comparison of DNA fragment separation results obtained for (a) a standard agarose slab gel, 4 mm thick and 4 mm wide and (b) an agarose gel 1 mm thick and 4 mm wide as formed by an etched silicon channel. Note the increase in both peak resolution and speed of separation in the thinner gel supported by the silicon substrate.

trend in improved resolution and speed in even narrower gels, down to 0.25 mm. However, difficulty arises in proper and repeatable sample injection in these narrower gels. This warrants further research and development in novel, precise, high-density, small-sample-volume injection.

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