FINAL REPORT**RADIATIVE INTERACTIONS WITH MICROMACHINED SURFACES:
SPECTRAL POLARIZED EMITTANCE****DE-FG02-88-ER 13964**

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PREFACE

This report covers work aimed at obtaining additional information on the electromagnetic emissions from heated, microstructured surface. Earlier work had established that thermal emission was a useful means for obtaining broad band information on the electromagnetic properties of these surfaces. Among the earlier results obtained was a demonstration that there was an increased amount of coherent radiation emitted from these structures. Also found was that the nature of the emission was dependent on the carrier concentration of the emitting material as well as the details of the geometry of surface structures. In light of this, a project was undertaken to construct a new emissometer based on a Fourier transform infrared spectrometer. The design of this system was completed in 1989-90 and the device was eventually built in 1991. In many respects, the system was very straightforward. By using a cryogenic pumping system, it was possible to minimize surface contamination of the heated silicon surfaces. The FTIR system caused a number of problems which greatly delayed the completion of the project. The project including: Professor Shlomo Hava, Visiting Associate Professor (permanent address is Department of Electrical Engineering, Ben-Gurion University of the Negev, Beersheva, Israel), Mr. Wolfram Urbanek, a graduate student in the Department, Mr. Akira Torao, Visiting Scientist from Kawasaki Steel Corp., Japan and Mr. Jacques Ip-Yam, a graduate student in the Department whose Master's Degree is the body of this final report. Also attached is a paper presented at A DOE Contractors meeting in Chicago on 8 May 1990.

Since the completion of this work, there has been a growth of interest in theoretical electromagnetic calculations of radiative interactions with gratings. Hava and Auslander have been particularly active in this area as a consequence of Hava's interaction with us. Cohen and Bockius present a paper on their calculations of electromagnetic scattering from microconfigured surface and found excellent agreement between their calculations and the experimental work of Hesketh et al. It appears that the experimental efforts have given rise to a growth of theoretical understanding of emission and scattering from microconfigured surfaces.

1. INTRODUCTION

1.1 GENERAL

The objective of this work is the study of thermal emission from heated lamellar silicon gratings. It is a follow up of previous work carried out here at the University of Pennsylvania by Hesketh *et al.* [1, 2, 3, 4, 5], Wang *et al.* [6, 7, 8, 9, 10], Zemel [11] and Bau *et al.* [12]. They observed interesting variations in the thermal emissivity from silicon lamellar microstructures. These variations depend not only on the microstructure geometry but also on the silicon doping concentration. Before their results are discussed in more detail, a brief discussion of the relevance of this research will be given.

Thermal radiation has been extensively studied as an important part of heat transfer in both science and technology. In fact, the understanding of blackbody radiation by Planck [12] at the beginning of the twentieth century led to the birth of quantum theory of matter. In general, most thermal radiation studies are carried out with bodies and surfaces having dimensions much larger than the wavelength. However, one can expect interesting phenomena to occur if the size of the radiating structures is comparable to the range of wavelengths being studied. For example, such studies are important when the roughness of surfaces and coatings is an important parameter. In the steel and optics industries for instance, surface smoothness of both metallic and non-metallic materials plays a critical role [13, 14, 15, 16, 17, 18]. In these studies, the surface is generally characterized by the roughness s defined by the rms. amplitude of the surface asperities. If the roughness to wavelength ratio s/λ is very small, the surface can be treated as a smooth specular reflector. As the ratio increases diffraction effects become important and at large s/λ values, Fresnel equations can be used to predict the distribution of emitted and/or reflected radiation. Various scattering theories together with statistical theories have been used to explain the properties of these surfaces [19, 20, 21, 22, 23].

Another way to study scattering effects from surfaces is to observe the emission or reflection properties of periodic structures such as diffraction gratings. Since their invention in 1786 [24], these optical elements, both metallic and dielectric in nature, have found numerous uses in a variety of applications, namely, spectroscopy, integrated optics, distributed feedback lasers and surface enhanced Raman scattering [25, 26]. The creation of an electromagnetic bandgap and enhanced stimulated emission has been predicted in periodic dielectric structures [27, 28].

In the microelectronics industry, with modern VLSI technology now requiring more and more complex chips with millions of devices, heat dissipation is becoming a limitation. Efficient liquid-cooled micromachined heat sinks have been designed [29, 30] for specific applications. Thus there is a strong need for a better understanding of thermal emission from small periodic structures. VLSI chips happen to have areas with substantial periodicity. Another area of importance to the semiconductor industry is the thermal processing of semiconductors such as rapid thermal annealing (RTA) which is used to activate dopants, anneal ion implantation damage and promote silicide formation. Monitoring the temperature and its distribution sometimes requires non-contact methods to avoid any possible contamination effects [31]. IR thermometers have already found their way into the market specially in the metal industry where the high temperatures of molten metals are monitored. However such non invasive devices have a significant limitation: their accuracy can be seriously impaired by the emissivity variation due to surface condition. For example if two objects are at the same temperature but one has a lower emissivity than the other the same IR thermometer will give a lower temperature reading for the

object with lower emissivity. Thus there is a need for emissivity compensation which can be very impractical [31, 32].

Studies have been conducted at the University of Pennsylvania, [1-11] under two DOE grants on the thermal emission from lamellar silicon gratings, both highly doped silicon (with near metallic free carrier densities) and intrinsic. The gratings were prepared using standard microfabrication processing techniques. Hesketh *et al.* [1-5] observed standing wave modes in the slots similar to organ pipe modes as well as some interactions which remain to be explained. Wang *et al.* [6-10], using undoped silicon gratings with near intrinsic carrier concentrations obtain results that gave strong indications of spatially coherent thermal emission from shallow gratings. They demonstrated that the s-polarized electromagnetic energy in deep lamellar gratings was confined to the fins of the dielectric rather than the slots based on agreement between the waveguide theory dielectric slabs and the experimental results. The s-polarized emission maxima agreed nicely with the corresponding cut-off wavelengths of dielectric waveguides.

However, there were a number of observations that could not be explained satisfactorily and thereby suggesting a continuation of the project. Hava *et al.* [33] designed an entirely new experimental set up to carry out the emissivity measurements. The new apparatus consisted of a vacuum chamber enclosing the heated sample to prevent oxidation of its surface (emissivity depends on the surface condition). A FTIR (Fourier Transform Infrared) spectrometer allowed a wider range of wavelengths to be measured: 2-25 μm vs. the original 2-14 μm . The thermal spectrum measurement, carried out by a computer controlled FTIR system, was much faster than the dispersive prism method used earlier; data collection time was reduced from over thirty minutes to about eight minutes. Another problem addressed by the new system was the dependence on a blackbody reference which introduced errors in Wang's experiments. Wang *et al.* found that errors were caused by differences in the sample and the blackbody reference temperatures. In the new set up, a flat smooth silicon element was used as a reference. The sample was designed to contain both the grating and the smooth reference. This minimized the temperature drift.

2. THEORY

2.1 THERMAL RADIATION AND BLACKBODY RADIATION

All substances above absolute zero temperature emit electromagnetic radiation continuously over the entire spectrum due to the molecular and atomic agitations associated with the internal energy of the body. The intensity of the emission depends not only on the temperature but also on the nature of the body surface and its bulk properties. When radiation is incident on a body, part of the radiation is reflected, part is absorbed and part is transmitted as demonstrated by the following equation:

$$\alpha + \rho + \tau = 1 \quad (2.1)$$

where α is the absorbance, ρ is the reflectance and τ is the transmittance. For opaque materials $\tau = 0$ and we obtain

$$\alpha + \rho = 1 \quad (2.2)$$

Thus an opaque material with low reflectance is a good absorber.

A blackbody is defined as a body which absorbs all incident radiation. If we consider a blackbody in equilibrium with an enclosure we see that the blackbody must be emitting as much energy as it is absorbing so as not to violate the second law of thermodynamics. This implies that a blackbody is also a perfect emitter. This is an application of Kirchoff's law.

$$\alpha = \epsilon \quad (2.3)$$

where α is the absorptivity and ϵ is the emissivity. This equation holds for any wavelength, direction or polarization

$$\alpha_\lambda = \epsilon_\lambda \quad (2.4)$$

$$\alpha(\theta, \phi) = \epsilon(\theta, \phi) \quad (2.5)$$

$$\alpha_{p,s} = \epsilon_{p,s} \quad (2.6)$$

where λ refers to wavelength, θ refers to polar angle, p and s refers to parallel and perpendicular polarizations respectively. Figure 2.1 shows the angle definitions and the two polarization states in relation to a grating sample which was the object of our study. Parallel polarization (p-polarization) refers to the state of the radiation with the electric field vector parallel to the plane of observation (defined as the plane formed by the normal to the surface and the direction of the radiation energy flow) and perpendicular polarization (s-polarization) denotes the state with the electric field perpendicular to the plane of observation.

Figure 2.1 Diagram of grating surface showing angle and polarization definitions. θ is the polar angle, ϕ is the azimuthal angle, p and s refers to parallel and perpendicular polarizations.

The amount of radiant energy emitted in a direction (θ, ϕ) at a wavelength λ per unit solid angle is defined as the directional spectral radiation intensity $I_\lambda(\theta, \phi)$. The total energy emitted over the entire spectrum is the directional radiant intensity $I(\theta, \phi)$ given by

$$I(\theta, \phi) = \int_{\lambda=0}^{\infty} I_\lambda(\theta, \phi) d\lambda \quad (2.7)$$

By means of quantum theory, Planck derived the spectral emissive power of a blackbody as a function of wavelength. This is known as Planck's radiation Law:

$$I_{b\lambda}(T) = \frac{C_1}{\lambda^5 (e^{C_2/\lambda T} - 1)} \quad (2.8)$$

where λ is the wavelength in meters, T is the absolute temperature in Kelvin, $C_1 = 3.742 \times 10^{-16} \text{ W-m}^{-2}$ and $C_2 = 1.439 \times 10^{-2} \text{ m-K}$

The Stefan-Boltzmann law shows that the total energy emitted by a black body has a fourth power temperature dependence. It can be derived by integrating equation (2.8) over all wavelengths to give the total emissive power per unit surface area as

$$I_b = \sigma T^4 \quad (\text{W-m}^{-2}) \quad (2.9)$$

where the Stefan-Boltzmann constant, $\sigma = 5.670 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$

Wien's displacement law gives the following relationship

$$\lambda_m T = 2.898 \times 10^{-3} \text{ mK} \quad (2.10)$$

where λ_m is the wavelength at which the maximum intensity occurs and T is the absolute temperature of the radiating surface. If the spectrum of a body can be measured, its temperature can be inferred from the value of the wavelength at the peak of the spectrum -- this can be checked against any other means of temperature measurement. In our particular case, the thermocouple temperature measurement obtained was compared to the value calculated by the application of Wien's displacement law to the thermal spectrum obtained.

2.2 RADIATION FROM REAL SURFACES

Most real surfaces do not behave like blackbodies. Real surfaces always radiate less than a blackbody at the same temperature. Since a blackbody is a perfect emitter, it serves as a standard with which the radiation characteristics of other surfaces are compared. We define the spectral

angular emissivity or directional spectral emissivity $\epsilon_\lambda(\theta, \phi)$ as the ratio of the energy emitted by the surface to the energy emitted by a blackbody with the same area, temperature and angle of observation.

$$\epsilon_\lambda = \frac{I_{s\lambda}(\theta, \phi)}{I_{b\lambda}(\theta, \phi)} \quad (2.11)$$

The same definition is used to denote the polarized nature of thermal radiation. The spectral angular polarized emissivity (SAPE) is given by

$$\epsilon_\lambda^p = \frac{I_{s\lambda}^p(\theta, \phi)}{I_{b\lambda}^p(\theta, \phi)} \quad (2.12)$$

$$\epsilon_\lambda^s = \frac{I_{s\lambda}^s(\theta, \phi)}{I_{b\lambda}^s(\theta, \phi)} \quad (2.13)$$

where P and S refers to parallel and perpendicular polarization. Emissivity values range between zero and one (or 0 - 100 %). In general, the emissivity depends on wavelength. However, a body can have a constant emissivity. Such a body is known as a gray body. In the next section, we will show that silicon can be considered as a gray body in the wavelength range of interest.

2.3 SILICON EMISSIVITY

Silicon offers a very convenient way to measure the thermal emissive properties of surfaces for several reasons. By using standard microfabrication techniques, we can build gratings with dimensions of the same order of magnitude as the emitted infrared radiation (2-25 μm). Specifically, etching technology which is the method used to fabricate the gratings, is a very well established micromachining technique. Also, high grade silicon with very smooth surfaces are readily available -- the smooth surface was used as a reference. By highly doping the silicon, we have a surface with near metallic properties as utilized by Hesketh *et al.* On the other hand, using undoped silicon which can be considered as a dielectric material since the carrier density at the temperature of operation is essentially intrinsic ($\approx 10^{16} \text{ cm}^{-3}$), we can observe emissions from a dielectric surface as carried out by Wang *et al.* Furthermore, conventional thin film deposition techniques make the deposition of a heating layer at the backside of the silicon sample rather straightforward.

2.3.1 NEAR-METALLIC SILICON GRATINGS EMISSIVITY

Metallic surfaces tend to become more reflective at long wavelengths, hence the emissivity decreases with increasing wavelength. Hesketh *et al.* measured the emissivity of highly doped silicon gratings of different periodicities and depths [1-4]. They observed maxima in the spectral angular polarized emissivity measurements for both P and S polarization.

For shallow gratings, some of the structures in the emissivity measurements were explained by Wood's anomalies and they were related to the excitation of the surface plasmons through coupling with the grating vector. Several explanations are given in the literature to account for Wood's anomalies [28-30]. According to Rayleigh [30], Wood's anomalies are due to the passing off of diffraction orders through the grazing angle occurring when the following relation is satisfied:

$$\sin(\theta_i) \pm 1 = \frac{m\lambda}{\Lambda} \quad (2.14)$$

where θ_i is the incident angle, λ is the wavelength, m is an integer and Λ is the repeat distance of the grating. The P anomalies could be accounted for by Rayleigh's explanation. The S anomalies could not be well explained. More recent theoretical results have accounted for many structures.

For deeper gratings Hesketh *et al.* observed standing electromagnetic wave modes corresponding to organ pipe like modes in the slots of the gratings.

2.3.2 DIELECTRIC GRATING EMISSIVITY

The dielectric properties of undoped silicon can be derived from Drude theory and free carrier absorption theory [1, 5, 31-33]. The dielectric constant ϵ of a solid depends on the contributions due to bound electrons (be), free carriers (fc) and phonon or lattice dispersions (la).

$$\epsilon = 1 + \chi_{be} + \chi_{fc} + \chi_{la} \quad (2.15)$$

The bound electron contribution occurs in the visible and higher frequencies and the phonon/lattice dispersion dominate in the far infrared range. For silicon under the conditions of our experiments, the free carrier dependence is the relevant term. It can be broken down into the electron and hole contribution:

$$\chi_{fc} = \chi_{fe} + \chi_{fh} \quad (2.16)$$

Using the Drude model, the contributions are given as follows:

$$\chi_{fe} = \frac{\omega_{pe}^2}{\omega(\omega + \frac{i}{\tau_e})} \quad (2.17)$$

$$\chi_{fh} = \frac{\omega_{ph}^2}{\omega(\omega + \frac{i}{\tau_h})} \quad (2.18)$$

where ω_{pe} and ω_{ph} are the plasma frequencies and τ_e and τ_p are the lifetimes of the electrons and holes respectively. The plasma frequencies can be expressed in SI units as

$$\omega_{pe}^2 = \frac{n_i e^2}{\epsilon \epsilon_0 m_e} \quad (2.19)$$

$$\omega_{ph}^2 = \frac{p_i e^2}{\epsilon \epsilon_0 m_h} \quad (2.20)$$

where n_i and p_i are the intrinsic carrier concentrations of silicon of electrons and holes respectively, ϵ is the dielectric constant of silicon, ϵ_0 is the dielectric constant of air, e is the electronic charge and m_e and m_h are the effective masses of electrons and holes respectively.

Assuming that $\omega\tau \gg 1$, we obtain

$$\chi_{fe} = -\frac{\omega_{pe}^2}{\omega^2} \quad (2.21)$$

$$\chi_{fh} = -\frac{\omega_{ph}^2}{\omega^2} \quad (2.22)$$

Since the silicon samples used in this study were heated to 550°C, the intrinsic carrier concentration dominates ($n_i = p_i = 3 \times 10^{16} \text{ cm}^{-3}$). The effective masses of the electrons and holes are $m_e^* = 1.28$ and $m_p^* = 0.95$ respectively as given by Jain [34]. Introducing these values into equations 2.19 and 2.20, we obtain $\omega_{pe} = 2.51 \times 10^{12} \text{ second}^{-1}$ and $\omega_{ph} = 2.92 \times 10^{11} \text{ second}^{-1}$. Using the relation

$$\omega = \frac{2\pi c}{\lambda} \quad (2.23)$$

we obtain the free carrier plasma wavelengths of $\lambda_{pe} = 751 \mu\text{m}$ and $\lambda_{ph} = 645 \mu\text{m}$. These values differ somewhat from Wang's values. However, the conclusion is the same: the result indicates that the dielectric constant is not affected by free carrier absorption in the infrared range of 2-25 μm . Thus the dielectric constant can be taken as a constant equal to 11.8.

Wang *et al.* evaluated the theoretical emissivity of a smooth silicon using Fresnel equations [5, 35-37]. This will be repeated here for arguments sake. Fresnel reflectivity equations for S and P polarizations for air to silicon interface are

$$R^s = \frac{\cos(\theta_i) - \sqrt{\underline{n}^2 - \sin^2(\theta_i)}}{\cos(\theta_i) + \sqrt{\underline{n}^2 - \sin^2(\theta_i)}} \quad (2.24)$$

$$R^p = \frac{\underline{n}^2 \cos(\theta_i) - \sqrt{\underline{n}^2 - \sin^2(\theta_i)}}{\underline{n}^2 \cos(\theta_i) + \sqrt{\underline{n}^2 - \sin^2(\theta_i)}} \quad (2.25)$$

where $\underline{n}$ represents the complex refractive index of silicon and θ_i is the angle of incidence. For an opaque material where the transmission is negligible, we can relate the emissivity and reflectivity using equation (2.2). Equation (2.3), derived from Kirchoff's law, states that the emissivity is equal to the absorptivity which, in turn, is related to Fresnel reflectivity R by

$$\alpha(\theta, \phi) = \epsilon(\theta, \phi) = 1 - \rho = 1 - |R(\theta, \phi)|^2 \quad (2.26)$$

In the normal direction, $\theta_i = 0^\circ$ and the Fresnel reflectivity equations (2.24) and (2.25) are simplified to

$$|R^s|^2 = |R^p|^2 = \frac{|\underline{n}^2 - 1|^2}{|\underline{n}^2 + 1|^2} \quad (2.27)$$

With the complex refractive index written as

$$\underline{n} = n + ik \quad (2.28)$$

we get an expression for the normal emissivity of the surface

$$\varepsilon(0^\circ, \phi) = \alpha(0^\circ, \phi) = \frac{4n}{(n+1)^2 + k^2} \quad (2.29)$$

As shown above by the free carrier absorption theory, the emissivity of silicon is a constant equal to 11.8. Thus, the refractive index of silicon is given by

$$\underline{n} = \sqrt{\varepsilon} = n + ik = 3.43 + i0.0 \quad (2.30)$$

The normal emissivity is then given by

$$\varepsilon(0^\circ, \phi) = \alpha(0^\circ, \phi) = \frac{4n}{(n+1)^2} = 0.7 \quad (2.31)$$

The experimental validity of this result is well established. Therefore, we decided to use a piece of smooth silicon as reference instead of a blackbody reference. We will come back to the possible advantages of this scheme when we discuss the design considerations of the experimental set up.

Wang *et al.* studied the thermal emissivity of undoped (therefore dielectric) silicon gratings. They found that for shallow gratings (1 μm) with long repeat distances, the emission were similar to smooth silicon. This was attributed to lack of spatial coherence over the period of the grating. However as the depth increases (3 μm) maxima were observed. It was shown from coupled wave theory that deeper gratings can couple energy between radiation modes better than shallow ones. The agreement of their data for s polarization emissivity with coupled wave theory strongly suggested that the thermal emission was spatially coherent.

Wang *et al.* observed that the s-polarized emission peaks for deep dielectric gratings can be explained with a waveguide model i.e., the S-polarization peaks coincide with the cut off frequencies of slab waveguides. This suggests that there is no (or very weak) coupling between the gratings for S-polarized emission. However, the P-polarized emission peaks could not be accounted for by waveguide theory. It was also observed that for the deep gratings none of the well known grating equation applied.

3. EXPERIMENTAL

3.1 SAMPLE DESIGN

We mentioned in the previous section that the emissivity of the grating will be referenced to a smooth surface instead of a blackbody as carried out by Hesketh *et al.* and Wang *et al.* . Although they were directly measuring the emissivity of the grating, one problem they occasionally faced was a temperature difference between the sample and the blackbody

reference. The measurements on the heated sample and the blackbody, which itself was non-perfect, were taken separately more than half an hour apart and it was difficult to keep the same temperature. Wang *et al.* observed a systematic error due to the sample temperature being higher than that of the blackbody. By having both the grating and the smooth reference on the same sample, we can ensure better temperature uniformity. The samples used in this study consisted of 2 cm x 3 cm rectangular pieces of silicon with a 1 cm x 1 cm area of vertically etched grooves. Figure 3.1 shows a front view picture of the sample. A heating layer of titanium silicide was formed at the back of the wafer.

3.2 SAMPLE FABRICATION

To make the grating area, vertical rectangular grooves were etched into the silicon. Figure 3.2 below shows a side view of the periodic gratings with the definitions of the parameters defining the geometry. H is the depth of the groove, L is the slot width and Λ is the repeat distance. Masks with repeat distances of 10, 14, 18 and 22 μm were available. In our experiment, we measured the emissivity for different repeat distances $\Lambda = 10$ and 14 μm for different depths H . Two etching techniques were used to make the gratings: plasma etching and wet chemical anisotropic etching. Plasma etching was more suitable for etching shallow grooves ($< 6\mu\text{m}$) whereas for the fabrication of deeper grooves ($> 6\mu\text{m}$), the anisotropic etching of (110) silicon was more appropriate. A discussion of each method is given in the next two sections. After the micromachining of the grooves, a heater was deposited on the backside of the sample. This was done by sputtering a thin film of titanium followed by rapid thermal annealing to form the silicide layer (TiSi_2). the final step was to cut the wafer into its rectangular shape.

Figure 3.1 Front view of sample

Figure 3.2 Cross-sectional diagram of sample showing the dimensional parameters

3.2.1 SHALLOW GRATINGS FABRICATION

Plasma etching has replaced conventional wet chemical etching in microelectronic fabrication as line width dimensions of circuits have shrunk down to micron and submicron geometries (VLSI) [38-40]. The main problem with wet chemical etching that makes it unsuitable for the fabrication of today's densely packed circuits is poor dimensional control. This is due to the fact that wet chemical etching, being inherently an isotropic process, allows undercutting beneath the masking layer thereby widening the linewidths. Other disadvantages of wet chemical etching include uneven etch due to bubble formation and masking layer attack by etching chemical.

On the other hand, plasma etching techniques allow the etching of very fine geometries with minimal undercutting while maintaining accurate control of feature size. Basically, a

plasma is a neutral ionized gas. It consists of electrons and charged ions which are highly reactive with the material to be etched. Initially, when a radio-frequency electric field is applied to a gas held at low pressure in a vacuum chamber, some electrons are knocked loose from the gas molecules. Because of their small mass the electrons are highly energetic. These electrons, accelerated by the electric field, collide with the gas molecules causing more ionization and gas molecule dissociation. As a result of these multiple reactions, ions, molecular fragments and excited molecules are formed. These particles are highly reactive. Thus gas together with rf power has to be continuously added to the system to maintain the plasma as the particles recombine or react with the material being etched. Some energy is emitted in the process as light giving the plasma a characteristic glow. The low pressure essentially reduces the collision rate of the charged particles thereby decreasing their recombination rates. The idea behind plasma etching is to select the appropriate gas which when in the plasma state produces reactive fragments that react with the material to be etched to form volatile products.

Plasma etching is used to etch a variety of surfaces such as silicon nitride, oxide, silicon, photoresist and aluminum. In our application, we are concerned with the etching of silicon. This is usually done with fluorine containing plasmas. Fluorine atoms formed in such plasmas react with silicon as follows:

The above equation does not give an accurate depiction of the complexity of the plasma etching process. The biggest challenge is how to obtain anisotropic etching. Certain chemicals such as CF_4 reacts very fast with silicon but the etching is isotropic i.e. it occurs in all directions equally. Anisotropy can be achieved if a live rf electrode rather than a grounded one is used. This technique is commonly referred to as Reactive Ion Etching (RIE). The live electrode creates a potential which causes the ions to bombard the surface perpendicularly with higher energy. Depending on how energetic the bombarding ions are, removal of material can occur in three ways. At high energies, the material is physically removed through erosion by the energetic ions in a process known as preferential sputtering. At low energies ions bombardment locally heats the substrate by loosening chemical bonds thereby promoting localized chemical reaction. Finally, in many plasma reactions a layer of inert polymer residue is formed on the substrate surface. This residue tends to slow down or stop the etching reaction. However, the ion bombardment can promote anisotropic etching by physically removing the residue on the surface and exposing the surface to the etchant species while leaving the passivating residue on the sidewalls intact. The literature shows that there are a significant number of gases (or mixture of) in use for the etching of silicon, silicon dioxide, silicon nitride, aluminum.

Figure 3.3 shows a schematic of the plasma etching system used in our experiment. It is a planar type reactor. A 13 KHz rf supply is connected between the top electrode and the bottom electrode which is grounded. The wafers are placed flat on the bottom electrode. The gas consists of a mixture of trifluorobromomethane CF_3Br , oxygen and nitrogen. CF_3Br has been found to give good anisotropy [38-40]. As mentioned earlier, fluorine atoms are the reactive species in the etching process. It was found that by adding bromine atoms to the mixture reduces the fluorine to carbon ratio (F/C) in the plasma. This has the effect of reducing the etch rate by forming polymer residues on the substrate surface. This residue also promotes anisotropic etching by accumulating on the sidewalls. The purpose of adding some oxygen into the mixture is to react with the carbon-bearing fragments to form carbon dioxide thus reducing fluorine consumption by carbon and increase the silicon etch rate.

Despite all the work done to understand the physics and chemistry of plasma systems, plasma etching is still highly empirical. Engineers have to work with a number of parameters. These are gas composition, gas pressure, rf power input, gas flow and temperature. In practice

each new plasma reactor has be characterized by a very long process of systematic tests to determine the optimal conditions. The fact that these parameters affect each other make the task very complicated. The reactor used in our experiment was a recent acquisition and we spent a long time before getting good anisotropy with reasonable etching rates. We also had problems with the masking film material. Aluminum was found to work well as a masking layer in the old plasma system that we had before. However, the new etch system would not etch with an aluminum mask (and gold which we tried also). Later it was found that using nichrome (NiCr) layer solved the problem. Complete details of the etching process including parameter values are given in appendix A.

Figure 3.3 Schematic of plasma etching system

3.2.2 DEEP GRATING FABRICATION

To fabricate deep gratings with vertical walls, the anisotropic etching of (110) silicon in 40 % by weight KOH solution was used. This technique is now widely used in micromachining -- the fabrication of 3-dimensional silicon structures whose mechanical properties are very useful in numerous sensing applications [41-44].

The (110) silicon wafer was initially oxidized to provide a protective oxide layer. The next step was to spin photoresist and align the mask for photolithography. In order to obtain vertical walls, the alignment of the channel with respect to the crystal planes is very important. Kendall reported that a selectivity of 400:1 for the (110):(111) planes can be obtained if the mask alignment with the wafer flat is precise to within 0.1° [41]. He found that the amount of

undercutting from each edge is approximately given by $H\theta/35$, where θ is the misalignment angle and H is the depth. Figure 3.4 shows the effect of misalignment. When the slot dimensions are small the misalignment ledges can be serious. In our case, the width of the slot was of the order of $10\text{ }\mu\text{m}$ and a small misalignment should not affect the shape of the gratings slot too much. There are several techniques to ensure proper alignment to the correct crystal plane. One method is to initially etch a tiny hole in the wafer. The hole etches into a hexagonal shape and self-stops. The edges of the hexagon correctly indicates the location of the (111) plane to which the channels must be aligned. This method was attempted but it was found that it was not very useful for alignment because the side of the hexagon was too short to represent a

Figure 3.4 Etch profile of (110) silicon showing effect of misalignment to wafer flat. Perfect alignment with the (111) edge gives perfectly straight slots whereas misalignment results in misorientation ledges.

reliable reference for alignment. It was like aligning a one foot ruler to a millimeter bar. Another method is to etch a long thin line on the wafer. After etching the misalignment ledges would show and alignment can be made to the real (111) plane. However this was not attempted. Instead, the somewhat crude method of 'eyeballing' was used. The reason that this technique was adopted was that we were already having problems in handling the rectangular shaped wafers (instead of regular rounded ones, the (110) wafers came in rectangular shapes of different sizes). For instance, the vacuum chuck in the aligner would not hold the wafer well thereby preventing any rotational or translational adjustment in high magnification visual field. For each wafer, the uncovered vacuum chuck holes on the wafer holder of the aligner had to be sealed by tape to ensure a reliable hold. The fact that the wafer sizes differed did not simplify the process. After uv exposure and development the exposed oxide was etched in buffered HF leaving the wafer ready for KOH etching. The details of the entire process is given in appendix B.

The misalignment effects were not severe. The misorientation ledges were insignificant as determined by visual inspection under the microscope. The walls appeared quite vertical and reasonably smooth.

3.2.3 HEATING LAYER FORMATION

A thin film of titanium ($1000\text{ }\text{\AA}$) was deposited on the wafer backside by sputtering. This was followed by rapid thermal annealing to form the heating TiSi_2 layer. Titanium silicide was selected because of its high resistivity and resistance to oxidation. Another benefit is that the silicide heating layer was effectively an integral part of the sample as the titanium atoms bond with silicon. This avoided any potential problem of having the heating layer separating from the silicon wafer and causing uneven heating.

3.2.4 WAFER CUTTING

The final step is wafer cutting. The (100) silicon wafer used for shallow samples were scribed parallel and perpendicular to the wafer flat and pressed by a metal roller. However, for (110) silicon used for deep gratings scribing and pressing could be done only for cutting along the (111) plane. It was not possible to scribe and press perpendicular to the (111) since there is no plane perpendicular to that plane as for (100) silicon. Any attempt to do so resulted in the breaking of the by-now precious sample. Instead a diamond saw was used. This method worked well although one has to be very careful when moving the wafer under the rotating blade.

3.3 EXPERIMENTAL SET UP

Figure 3.5 below shows the experimental set up. It was designed and built by Torao *et al.* The sample, held by a molybdenum holder with low resistivity and good resistance to oxidation, is enclosed in a high vacuum chamber (1×10^{-3} mbar). It is heated by connecting a power supply across it. A water cooling jacket made of a coil of copper tubing surrounds the entire sample assembly except for a window in the optical path from the sample to the detector. This prevents any reflections of energy by the walls of the vacuum chamber from falling onto the detector by absorbing any radiation outside the field of view of the detection path. It also serves to keep the assembly from getting dangerously hot. By turning the rotational feedthroughs, the sample is rotated in both the polar (θ) and azimuthal (ϕ) directions. The thermal radiation from the heated sample passes through a slit S1 located inside the vacuum chamber and then passes through a KBr window to another pair of slits, S2 and S3. The sample surface is located at a distance equivalent to the focal length of the spherical mirror. The radiation is reflected by the spherical mirror onto a flat mirror tilted at 45° to the horizontal. After this stage, the signal is in a parallel beam and it goes into the MIDAC FTIR interferometer. The latter is a Michelson type Fourier Transform interferometric spectrometer with a beam splitter and a moving mirror. The moving mirror changes the path difference of the split beam thus giving an interference pattern. The position and velocity of the moving mirror is monitored by a HeNe laser signal passing through the interferometer and is measured by a pair of quadrature phase detectors. The output of the interferometer is the intensity as a function of mirror displacement. The output of the interferometer is focused by a spherical mirror onto the window of a liquid nitrogen cooled mercury cadmium telluride (MCT) detector supplied by Judson-Infrared. The signal from the MCT detector is amplified and fed into the computer which processes the data to give the IR spectrum. The frequency spectrum is in effect constructed by taking the Fourier transform of the intensity as function of the mirror displacement. The computer communicates with the interferometer via an interface card. The number of repeated scans and the resolution of the interferometer can be selected to achieve the best spectra. Measurement of the spectrum is very fast: 3000 repeated scans were carried out in about eight minutes. The interferometer and the MCT detector are housed in a dry box continuously flushed with dry nitrogen. This is to prevent any absorption errors due to gases in the atmosphere such as carbon dioxide and water vapor. Furthermore, the beam splitter assembly in the interferometer is very susceptible to damage by moisture. To polarize the radiation, an infrared polarizer (KRS-5) is placed after S2 in the optical path. Both parallel and perpendicular polarizations are obtained by rotating the polarizer through 90° . Each time a new sample was installed in the system, the optical path was aligned by using an external HeNe laser and a mirror. The temperature was measured by a thermocouple (type K) in contact with the sample inside the vacuum chamber.

The emissivity measurement is given by

$$\epsilon_{\lambda}(\theta, \phi) = \frac{I_{g\lambda}(\theta, \phi) - I_{bg\lambda}}{I_{s\lambda}(\theta, \phi) - I_{bg\lambda}} \quad (3.2)$$

where $I_{g\lambda}(\theta, \phi)$ was the spectral intensity of the gratings, $I_{s\lambda}(\theta, \phi)$ was the spectral intensity of the smooth reference and $I_{bg\lambda}$ was the spectral intensity due to the background. The background radiation is the radiation to the surroundings in the absence of any heated source. It was subtracted from the spectrum obtained for each heated surface.

Figure 3.5. Schematic diagram of experimental set up

3.4 DESIGN CONSIDERATIONS

3.4.1 SIGNAL TO NOISE RATIO

One of the major considerations was to ensure a high signal to noise ratio. In order to have a high signal, the amount of radiant energy coming from the heated sample has to be high. From Stefan-Boltzmann law, the power emitted per unit area depends on the fourth power of the temperature. Thus the higher the sample temperature, the higher the total energy emitted. The amount of power required by our power supply can be estimated by calculating the total power emitted by the sample since at equilibrium, the total energy emitted is equal to the total energy supplied to heat the sample assuming that all the heat losses occur through radiation from the sample. Stefan-Boltzmann law is given by

$$P = \epsilon \sigma T^4 \quad (3.3)$$

where ϵ is the emissivity of silicon, σ is the Stefan-Boltzmann constant equal to $5.670 \times 10^{-12} \text{ Wcm}^{-2}\text{K}^{-4}$. At 550°C ($T=823 \text{ K}$), taking ϵ to be 0.7, we get the power emitted per unit area is equal to 1.82 Wcm^{-2} . The sample dimension was $2 \text{ cm} \times 3 \text{ cm}$. Since both sides are emitting, the total emitting area is 12 cm^2 . This gives a total power of 21.85 W . In reality, a fraction of the energy supplied is used to heat the metal holder which itself conducts heat away from the sample. The amount of power conducted away from the sample will be neglected at this point because its estimation is non-trivial since the shape of the conducting structure itself is not simple. On the other hand, convective losses can safely be neglected since the assembly is in vacuum. Nevertheless, a significant portion of heat is also radiated by the metal holder. This is minimized by having the holder highly reflective by polishing its surface (this effectively reduces its emissivity). But, since the holder surface area is quite large compared to the sample area, we estimated that the total power requirement should be at least 50 W .

A question that arose was what kind of power supply was needed to supply at least 50 W . Particularly we were concerned about what voltage and current values were needed. At room temperature, the resistivity of silicon is high. Thus, the resistance of the sample was essentially determined by the resistance of the silicide heating layer. Typically the resistance of the sample was about 15Ω at room temperature. However as the sample is heated the resistivity of the silicon decreases dramatically. At a certain temperature (about 300°C), we observed that the resistivity of the silicon would suddenly decrease very rapidly so that the overall sample resistance would drop dramatically to about 1.5Ω . This behavior showed the onset of the region where the intrinsic carrier concentration started to dominate over the extrinsic carrier concentration. When this happened, in order to supply enough power to the sample, the power supply must be able to deliver high currents. For example, to deliver 50 W to a 1.5Ω resistor, the current required is 5.8 A . Torao *et al.* used a power supply rated at $36\text{V}-6\text{A}$. But we found that at the maximum current of 6 A , the temperature attained was only 400°C . At this temperature, it appeared that the signal to noise ratio was not satisfactory. A new power supply ($60 \text{ V}-14 \text{ A}$) was purchased to increase the sample temperature. The new power supply gave a wider current range to work with (remember that as the sample gets hotter the resistance goes further down and the current requirement jumps up). The new supply was capable of controlling the current to within 1 decimal place. It was extremely important to adjust any temperature drift during data collection. To obtain a temperature of 550°C typical values of voltage and current were 9.9 V and 7.2 A (corresponding to a sample resistance of 1.4Ω). The power delivered was 71.3 W . We could have operated at a higher temperature but we also have to make sure that the current carrying capacity of the leads (12 A) was not exceeded.

P gives the total energy emitted by the of the sample. To estimate the amount of energy reaching the detector depends on the size of the slit or the solid angle subtended by the slits. However this angle cannot be made too large for it will affect the resolution of the measurement of the angular dependence of the emissivity. Hava *et al.* designed the system so as to have an angle of 1° from the horizontal.

3.4.2 TEMPERATURE UNIFORMITY

In the initial design by Hava *et al.*, there were two optical paths for measuring the thermal emission from the smooth and the grating surfaces as shown in Figure 3.6. This method had the merit of not having to move the sample at one temperature value thereby avoiding any possible disturbances caused if the sample had to be moved for each measurement. In one setting, the emission from both the smooth and grating surface can be obtained by simply adjusting the slits. However, a systematic error can be introduced if the optical paths are not identical. A small difference in the path could seriously alter the signal reaching the window of the detector which itself is very small and consequently has to be precisely aligned. Since the data collected using this method did not seem to be consistent with the results expected from Wang's data, we decided to change to a new technique where only one path was used for both measurements.

Figure 3.6. Diagram showing the two optical paths for measuring the smooth and the grating emissivity in old system. A systematic error will occur if the two optical paths are not similar.

In this method, only the bottom optical path was used. Figure 3.7 shows the sample holder and the sample. The sample was rotated through 90° to measure the spectrum from both the grating and smooth surfaces as depicted by figures 3.7 (b) and (c). Observation of the thermocouple reading indicated that there were no drift in temperature on rotation. However, some of the data suggested that there might be a temperature drift between the grating and the smooth surface. In particular in some instances the temperature of the grating appeared to be lower than the smooth reference. However, one may argue after all that since the emissivity of a grating surface is generally higher than a smooth surface it is reasonable to expect the grating temperature to be slightly smaller than the smooth surface. However, the fact that silicon has very good thermal conductivity, the size of the grating surface is small compared to the smooth surface and the distance between the radiating surfaces is relatively short leads us to believe that the temperature difference should be rather small.

Figure 3.7. Side, (a), and front, (b) and (c), views of sample and holder. (b) and (c) are positions for grating and smooth surface measurements. Full circles represent observation area.

To illustrate the effect of temperature drift on emissivity measurements, the emissivities of surfaces at lower temperatures than a reference at 823 K (550°C) was calculated using Plank's spectrum distribution (equation 2.8). This is plotted in figure 3.8. It can be seen that emissivity increases with increasing wavelength. While a 5 degree difference may be tolerable, a 10 degree difference causes a significant shift in the emissivity. It should be noted that if the reference is at a lower temperature than the surface to be measured then the emissivity curve will be reversed and have a negative slope instead.

Figure 3.8. Graph showing the effect of temperature difference between a blackbody sample and a blackbody reference on emissivity. The reference is at 823 K (550 °C) and the sample is at 820 K, 818 K and 813 K.

To calibrate the spectrometer, the transmission spectrum of a standard polystyrene film was taken as shown in Figure 3.9. This was carried out by taking the ratio of the spectrum of a smooth silicon surface at 450 °C and the spectrum of the same source but with the polystyrene reference in the optical path (at S2 in this case). The transmission spectrum shows the location of the characteristic absorption wavelengths corresponding to the bonds in the polystyrene chemical structure. The measured spectrum agrees well with the standard spectrum.

Figure 3.9. Measured transmission spectrum of polystyrene for calibration purposes. It agrees well with the standard spectrum.

4. EXPERIMENTAL RESULTS

It was found that the system needed to be stabilized for a long period of time (about 2 hours) before reliable data could be obtained. This was done by turning on both the spectrometer and the heater circuit for a couple hours with a generous flow of dry nitrogen inside the dry box prior to measurement. The apparatus has very good resolution and was consequently susceptible to small traces of moisture or water vapor contaminants. Each time the dry box was opened to rotate the polarizer, a waiting time of about half an hour was required in the dry nitrogen flush before the next measurement was carried out. The measurements for the grating and smooth surface were carried out consecutively with minimum time between them. Small adjustments in the power delivered were required to compensate for temperature drifts which were of the order of $\pm 2^\circ \text{C}$.

The experimental results are presented below. Figures 4.1-4.9 show the data for a grating at 450°C with $\Lambda = 10 \mu\text{m}$ and $H = 6 \mu\text{m}$. From figures 4.1, 4.2, 4.5 and 4.6, it can be seen that the intensity of the background radiation was quite large compared to the radiation due to the heated sample especially in the longer wavelength region. Figures 4.3 and 4.7 show the P and S polarized spectrum respectively, after subtraction of the background radiation. The emissivity curves, figure 4.4, 4.8 and 4.9, were obtained by taking the ratio of the grating spectrum to the smooth spectrum for each polarization. Structures are clearly visible for both polarizations. The graph for the S polarization, figure 4.8, shows very distinctly the presence of fairly equally spaced maxima and minima. There are maxima at wavenumber values 1000, 1500, 2000 and

2600 cm^{-1} . Using coupled wave theory, Wang calculated S polarized maxima at 1000, 2000 and 2700 cm^{-1} for $\Lambda = 10 \mu\text{m}$, $H = 2.75 \mu\text{m}$, reproduced here in figure 4.10(a) Figure 4.10(b) is a replot of our experimental data with the same wavenumber range as Wang's for comparison. Wang also experimentally measured maxima at 1000 and 2000 cm^{-1} for $\Lambda = 10 \mu\text{m}$, $H = 3 \mu\text{m}$. Except for the 1500 cm^{-1} peak, both of Wang's calculated and experimental results agree nicely with our data. The agreement between our experimental results and Wang's simulation based on couple wave theory suggests that the emission is spatially coherent. The 1500 cm^{-1} maximum could be associated with a depth mode since this corresponds to $6 \mu\text{m}$ deep standing wave. The data for P polarization has peaks at 1000, 1200, 1700, 2300, 3000 and 3500 cm^{-1} . Further analysis is required to adequately explain these P polarized observations. Judging from the additional structures, it appears that the new system has more resolution than Hesketh's and Wang's. It is also very interesting to note from figure 4.9 that the maxima of the S polarized emissivity curve correspond to the minima of the P polarized emissivity curve and vice versa. This was not observed by Wang *et al.*, again calling for further experimental and theoretical development.

Figure 4.1 Measured total normal P-polarized spectrum for grating surface at 450°C, $\Lambda = 10 \mu\text{m}$, $H = 6 \mu\text{m}$ and background radiation.

Figures 4.11 (a) and 4.11(b) show the polarized emissivities for a $\Lambda = 14 \mu\text{m}$, $H = 2.5 \mu\text{m}$ sample at 550° C. Structures are clearly present for both polarization readings. The S polarized data has peaks at 1300, 2000 and 2600 cm^{-1} . Figure 4.12 show a comparison between our results and Wang's experimental results for $\Lambda = 14 \mu\text{m}$ and $H = 3 \mu\text{m}$. Wang observed peaks at 1400 and 2000 cm^{-1} for the same repeat distance and $H = 3 \mu\text{m}$. It would be interesting to carry out coupled wave calculations, similar to Wang's, on this dimension. The P polarized data has peaks (although not as discernible as the S data) at 1300, 2100, 2800 and 3300 cm^{-1} . Wang's P polarized data for $\Lambda = 14 \mu\text{m}$ and $H = 3 \mu\text{m}$ has peaks at 1200, 1900 and 2800 cm^{-1} which is acceptable agreement. We observed that our S emissivity was higher than the P emissivity, which is the reverse of Wang's data. Further investigation is required.

Figure 4.2 Measured total normal P-polarized spectrum for smooth surface at 450 °C, $\Lambda = 10 \mu\text{m}$, $H = 6 \mu\text{m}$ and background radiation.

Figure 4.3 Normal P-polarized spectrum for grating and smooth surface at 450 °C, $\Lambda = 10 \mu\text{m}$, $H = 6 \mu\text{m}$, after subtracting background radiation.

Figure 4.4 Normal P-polarized emissivity for grating at 450°C, $\Lambda = 10 \mu\text{m}$, $H = 6 \mu\text{m}$.

Figure 4.5 Measured total normal S-polarized spectrum for grating surface at 450°C, $\Lambda = 10 \mu\text{m}$, $H = 6 \mu\text{m}$ and background radiation.

Figure 4.6 Measured total S-polarized spectrum for grating at 450° C, $\Lambda = 10 \mu\text{m}$, $H = 6 \mu\text{m}$ and background radiation.

Figure 4.7 Normal S-polarized spectrum after subtracting background radiation for sample at 450°C, $\Lambda = 10 \mu\text{m}$, $H = 6 \mu\text{m}$.

Figure 4.8 Normal S-polarized emissivity for grating at 450°C, $\Lambda = 10 \mu\text{m}$, $H = 6 \mu\text{m}$

Figure 4.9 Normal S and P polarized emissivity for grating at 450°C, $\Lambda = 10 \mu\text{m}$, $H = 6 \mu\text{m}$.

Figure 4.10 (a). Wang's S polarization coupled wave calculation for $\Lambda = 10 \mu\text{m}$, $H = 2.75 \mu\text{m}$. Experimental result for normal S polarized emissivity for $\Lambda = 10 \mu\text{m}$, $H = 6 \mu\text{m}$. This is figure 4.8 replotted with same horizontal scale as Wang's calculations for comparison.

Figure 4.11 Normal S and P polarized emissivity for grating at 550°C , $\Lambda = 14 \mu\text{m}$, $H = 2.5 \mu\text{m}$.

Figure 4.12 Normal polarized data for $\Lambda = 14 \mu\text{m}$, $H = 2.5 \mu\text{m}$ compared to Wang's experimental normal polarized emissivity for $\Lambda = 14 \mu\text{m}$, $H = 3 \mu\text{m}$.

5. CONCLUSIONS

The normal polarized emissivity of undoped silicon gratings of different dimensions was measured with the new emissometer. The data obtained for $\Lambda = 10 \mu\text{m}$, $H = 6 \mu\text{m}$ and $\Lambda = 14 \mu\text{m}$, $H = 2.5 \mu\text{m}$ clearly indicated that the structures were in good agreement with earlier data on S-polarized emission for a grating with $\Lambda = 10 \mu\text{m}$ and $H = 3 \mu\text{m}$ and Wang's coupled wave theoretical calculations for a similar sized grating. The data for $\Lambda = 14 \mu\text{m}$ agreed well with Wang's experimental results.

The normal polarized results obtained demonstrate that the new emissometer is operational. The next step is to fabricate more samples of different dimensions to obtain a wide set of data. A study of the angular variation of emissivity should yield very interesting results. These results together with further theoretical studies should give way to a better understanding of the phenomena.

Appendix A

Shallow Grating Fabrication -- Plasma etching

P (100) wafers of resistivity 5 - 25 Ω -cm were used. In general a batch of 5 wafers were processed each time. The steps involved in the entire procedure are given below.

A.1 Wafer Cleaning

Heat in a mixture of H_2O_2 and H_2SO_4 [1:2] to 120°C for 10 minutes
Overflow rinse in DI water for 1 minute
Dip in dilute HF [1:25] for 15 seconds
Overflow rinse for 1 minute
Spin dry.

A.2 Metal deposition

Load wafers in planetary configuration.
Rough pump.
Cryopump down to pressure of
Use electron beam evaporator to deposit nichrome layer onto wafers.
Evaporation time = 4 minutes
Thickness of film = $2\Delta f/D$
where Δf is oscillation frequency of crystal and D is density of NiCr = 8.2 gcm^{-3}

A.3 Align grating

Apply HMDS for 5 minutes.
Spin photoresist at 4000 rpm for 20 seconds.
Soft bake at 90°C for 3 minutes.
Align grating mask with wafer flat.
Expose and develop.
Hard bake at 125°C
NiCr etch
310 g ceric ammonia nitrate
1970 ml. H_2O
120 ml. HNO_3
Rinse in DI water
Strip resist
Rinse in DI water
Spin dry

A.4 Plasma Etching

Load samples flat.
 CF_3Br flow rate = 120
 O_2 flow rate = 55
 N_2 flow rate = 22
Throttle to 480 mTorr
Power = 400 W
Etch rate = 900 Å/minute (5000 Å/minute was obtained later!)

A.5 NiCr etch

Etch until all NiCr goes away. Heat if necessary

Rinse in DI water

- A.6 Back side heating layer
Clean wafers ($\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$)
Titanium sputter 1000 Å on back side
Rapid thermal anneal (900°C for 20 seconds)
- A.7 Cut wafers
Scribe wafers
Roll to break along crystal planes

Appendix B Deep Grating Fabrication

P (110) wafers of resistivity 25-40 Ωcm with the (111) direction indicated by a notch were used. These wafers were rectangular in shape and each wafer differed in size.

- B.1 Wafer cleaning
Same as A.1
- B.2 Oxidation (1 μm thick)
Furnace temperature 1100 ° C
Water temperature 95 ° C
Push in dry oxygen
Dry oxide for 5 minutes
Wet oxide for 2.5 hours
Dry oxide for 3 minutes
Pull in dry nitrogen
- B.3 Mask alignment
Spin positive photoresist
Soft bake at 90° C for 5 minutes
Align mask edge with (111) edge visually so that channels on mask are as parallel as possible with (111) edge (split field technique not appropriate here unfortunately)
Expose and develop
Hard bake at 125° C
- B.4 Oxide etch
Etch in 10 % buffered HF until all exposed oxide is removed
Rinse in DI water
Strip resist
Rinse in DI water
- B.5 Etch grooves
Dip in dilute HF for 15 seconds to remove native oxide
Immediately immerse in 40% by wt. KOH solution at 50°C
Depth = etch rate x time
Rinse in DI water
- B.6 Remove oxide
Immerse in BHF until dewetting occurs
- B.7 Backside heating layer
Same as A.6
- B.8 Wafer cut
Scribed and roll wafer parallel to the (111) edge
Perpendicular to the (111) edge, cut wafer with a diamond saw

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ENERGY AND MASS TRANSPORT IN MESOSCALE STRUCTURES

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ABSTRACT

Using current micromachining methods, structures with lateral scales, S , of $150 \text{ nm} \leq S \leq 150 \text{ } \mu\text{m}$ and heights, H , of $15 \text{ nm} \leq H \leq 150 \text{ } \mu\text{m}$ can be made. Energy and mass transport in this dimensional regime has been limited so far because of manufacturing difficulties. Recent results on the spectral angular polarized thermal emission from relatively shallow gratings, i.e. $H \sim 3 \text{ } \mu\text{m}$, with repeat distances, Λ , comparable to the emitted wavelength, λ , i.e. $0.1\lambda \leq \Lambda \leq 10\lambda$, is discussed. Other studies on very thin channels, $H = 0.48 \text{ } \mu\text{m}$ and $3.0 \text{ } \mu\text{m}$, are also discussed. It has been argued that flow size effects should only arise when fluid molecular diameters are comparable to channel size. Nevertheless, our experimental results deviate from the classical Navier-Stokes friction law predictions when $H \leq 5 \text{ } \mu\text{m}$. Additional experimental and theoretical studies are needed to clarify the status of transport in this regime.

INTRODUCTION

The micromachining of various electronic materials, particularly silicon, is now a well developed art. Photolithographic batch processing, anisotropic etching of the semiconductor materials using both crystallographically selective wet chemical etches and reactive ion dry etches has made it possible to construct a wide variety of both simple and sophisticated electronic and physical structures at relatively low cost (ignoring the huge capital investment in clean rooms and photolithographic equipment)¹. For well over a decade, there has been an ongoing program here at the University of Pennsylvania to develop methods for studying some questions that were either difficult or impossible to address without structures manufactured with these micromachining techniques. In the past decade, we have addressed the question of energy, momentum and mass transport involving structures whose smallest dimensions have been $\leq 50 \text{ } \mu\text{m}$. The two most intensively studied subjects here have been thermal emission from periodic structures, i.e. gratings, and the flow of liquids in micron and sub-micron high channels. The emphasis of these studies has been largely experimental since the models for electromagnetic interactions with deep grating and fluid flow in thin channels have not been subject to full experimental verification. It appears that these models are either too simplistic or inadequate to account for the experimental results. We conclude that a re-evaluation of existing grating theory, especially in the conical diffraction mode, is needed and a re-examination of the assumptions leading to the Navier-Stokes relations for very narrow channels would be desirable.

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SPECTRAL ANGULAR POLARIZED EMISSION

In earlier work on heavily doped silicon structures, we had observed resonant radiative emissions corresponding to standing waves in the slots of the grating^{2,3,4,5}. These resonances were dubbed "organ pipe modes" to express their standing wave character. In these initial studies, it was shown that strong resonances would occur in the deep slots of heavily doped lamellar grating produced by the wet chemical etching of <110> silicon. An integrated heater was constructed on these samples which made it possible to raise the temperature as high as 500°C and control the temperature relative to a home-built black body source to within a few degrees Celsius. Emission measurements were conducted over the spectral range $3\ \mu\text{m} \leq \lambda \leq 14\ \mu\text{m}$. Both S and P polarization measurements were conducted (See figure 1 for the orientation of the polarization vectors relative to the plane of observation).

Figure 1: Schematic showing the dimensions, angles and polarizations of the grating

We have continued these studies on undoped silicon in an attempt to examine the extent to which the electromagnetic fields in the slots and fins of the lamellar couple to each other. Both flat surfaces and those with gratings were investigated. The lamellar gratings where the ratio of the emitted wavelength, λ , to depth, H , ranges from $0.05 \leq \lambda/H \leq 5$. The ratio of H to the periodicity of the grating, Λ , was $0.14 \leq H/\Lambda \leq 6$. The grating structures were heated to temperatures ranging from 300°C to 400°C and grating no substantive difference in the emissivity from either temperature was observed. The measurements were carried out

over the wavelength range of $3\ \mu\text{m} \leq \lambda \leq 14\ \mu\text{m}$ using a Perkin Elmer 112 NaCl prism spectrometer and an EG&G-Judson $14\ \mu\text{m}$ cut-off HgCdTe photoresistor. The emission from the silicon grating was compared to that from a home-built black body source. Apparently the source had an effective emissivity of ~ 0.90 which introduced a systematic error into the readings. The magnitude of the error was established by conducting measurements on a flat silicon sample. The remainder of the measurement system was quite ordinary. A lock-in amplifier was used with the photoconductive HgCdTe detector, and a PC based system was used to control the goniometer stepper motor for the polar angular measurements, digitize the lock-in amplifier signal, process the information and plots the data.

Figure 2: SAPE(θ , P, 90° , 400°C) for selected wavelengths. The shaded regions correspond to the forbidden zones calculated from Eq. 1. The o are the approximate experimental Rayleigh limits.

Both experimental and theoretical studies were conducted for emission normal to the surface and for the polar angular dependence θ of the emission relative to the normal direction. The experiments demonstrated that the radiant flux emitted from the lamellar structure is highly dependent on the azimuthal angle, ϕ (See Figure 1). When the wavelength and the periodicity of the grating for $\phi = 90^\circ$ (see Figure 1) support two diffracted orders, there will be a region between the allowed orders where no diffraction is allowed. This angular region, $\Delta\theta$, is defined by two angles, θ_1 and θ_2 obtained from the limiting diffraction equation,

$$\sin\theta_j = 1 - m\frac{\lambda}{\Lambda}, \quad j = 1, 2$$

in the $\Delta\theta$ range, the emission of the p polarized radiation is enhanced, giving rise to plateau as illustrated in Figure 2. Because this is a "forbidden zone", the propagation vectors for diffracted rays must be complex and would then decay within the grating zone causing an incident plane wave to be totally reflected. Because these surface waves are exponentially decaying, under time reversal they will become emitting states. This can be appreciated by recognizing that while the decaying surface modes cannot sustain a propagating state in the crystal, nevertheless, they will contain surface bound photons by Bose-Einstein statistics. As a result, these emitting (decaying) modes are what we propose as the source of the photons that cause the observed plateau maximum. The amplitude of the maximum is dependent on H . There is an interesting variation with θ as the λ approaches Λ . The "sag" seen in the SAPE for $\lambda = 9 \mu\text{m}$ might be accounted for by the limited range of the surface modes that contribute to the plateau. This, like so many other processes we have been examining, needs additional theoretical and experimental study.

For $\phi = 0^\circ$, the plane of observation lies along the fins and slots. This direction corresponds to what is called the conical diffraction direction. Some typical data illustrating this behavior is shown in Figures 3.

Figure 3 SAPE ($\theta, S, 0^\circ, 400^\circ\text{C}$) normalized with respect to the flat surface ;
 $\Lambda = 10 \mu\text{m}$, $H = 3 \mu\text{m}$, $L = 6.5 \mu\text{m}$

Figure 4: Variation of the threshold angle for SAPE($\theta_t, \lambda, S, 0^\circ, 400^\circ\text{C}$).

To better illustrate the behavior, we normalized the SAPE from the $H = 3 \mu\text{m}$, $\Lambda = 10 \mu\text{m}$ grating against the corresponding flat surface SAPE. As can be seen, there is a fairly sharp threshold corresponding to a first order process and a weaker second order threshold. In Figure 4, we plot the threshold angle for the onset of these processes against the wave number of the radiation. The empirical functional dependence we obtain is

$$2mK(\sec\theta_t - \frac{1}{2}) = k_t \quad 2)$$

where the subscript t refers to the threshold values. The agreement between this relation using for different

grating repeat distances is well illustrated in Table I. In this Table, values of the slope obtained from Figure 3 are compared against corresponding values

of the slope calculated from the known values of Λ .

The agreement between the measured and theoretical slopes based on these quite acceptable

So far, we have been unable to find a diffraction or standing wave condition corresponding to this empirical law. However, it does appear that the mechanism involved depends critically on the presence of surface waves in the vicinity of the grating. A re-examination of

Hesketh's data suggests that a similar process is occurring in some of his gratings⁶. The strength of the emission is rather surprising as is the tendency of the emission to flatten off in the plateau region.

Table I:

	Λ	$2m/\Lambda$	Slope	Λ_{eff}	% error
□	3	0.333	0.328	3.05	1.64
◆	5	0.200	0.190	5.25	4.76
■	2.5	0.400	0.385	2.60	3.85
●	7	0.143	0.129	7.77	9.91
⊠	3.5	0.286	0.262	3.81	8.13
⋈	11	0.091	0.085	11.83	7.02

A series of calculations were performed for s polarized, $\phi = 90^\circ$, radiation using existing coupled wave and Bloch wave models for lamellar gratings⁷. The coupled wave calculation in the normal direction demonstrated a striking agreement with the experimental normal direction spectral emission data as indicated in Figure 5. The angular dependence was in quite good agreement with the experimental data except for the shorter wavelengths where the overall validity of the model becomes questionable. This is the region where more than two spectral diffraction orders can be maintained. Numerical calculations for the other polarizations diverged, especially when more than two diffraction orders are present. Because they were so much more difficult, no further attempt was made at this time.

Based on these experiments and calculations, we conclude that thermally emitted radiation from these dielectric gratings has a significant degree of

spatial coherence. It will be important to conduct a direct measure of coherence in the near future. The implication for heat transfer and electromagnetic interaction with microstructures is intriguing and will be considered further in the Discussion and Conclusions. It should be noted that the inverse experiment is being developed here and results are expected shortly.

Fig. 5: Normal S polarized emission. $\Lambda = 10 \mu\text{m}$,
a) coupled wave result; $H = 2.75 \mu\text{m}$, $L = 6.5 \mu\text{m}$;
b) Experimental result; $H = 3.0 \mu\text{m}$, $L = 6.5 \mu\text{m}$

FLUID TRANSPORT IN MICRON AND SUBMICRON CHANNELS

The study of fluid flow in well defined microchannels is in its infancy. The advances in micromachining methods developed over the past three decades in the microelectronics industry now make it possible to construct flow cells with which to examine fluid flow at a scale never fully possible before¹. In recent years, many researchers have begun to exploit planar photolithography to develop a range of microsensors that are small and complex⁸. From this base of microstructure research, interest has been growing on micromechanical systems. This work includes microactuator systems and micromechanical devices, such as gear trains, cantilevered vibrators, etc., that were reviewed originally in a NSF Workshops on Robotics and Teleoperators⁹. Since this first meeting in 1988, there has been two additional Workshops on Micromechanics with a strong emphasis on actuation. However, there has not been a corresponding effort in fluid flow in structures whose minimum dimension is of the order of microns or less. Other than our work, the current research on fluid flow through micromachined meso-scale structures is directed toward thermal management of electronic structures^{10,11,12}. In addition to understanding the fundamentals of flow in small channels, micromachining makes it possible to design and construct deterministic quasi-two dimensional random and non-random flow structures which can emulate corresponding porous media. Because the structures are deterministic, they offer the possibility of developing a more quantitative theoretical understanding of flow in such media. There may be device opportunities for biological measurements in these systems¹³.

In the past several years, a cross-disciplinary activity at the University of Pennsylvania has been directed at studying the behavior of fluids flowing in micromachined channels. Currently,

we are investigating Newtonian fluid transport of single phase liquids in meso-scale channels. The mesoscale regime consists of dimensional scales, S , that are large compared to atomic/molecular dimensions, a_0 , but small compared to macroscopic length scales, L , i.e. $L \gg S \gg a_0$. In many branches of contemporary physics there is evidence that new phenomena arise at these intermediate length scales¹⁴. Also, the theoretical studies by Eringen and coworkers on micropolar fluids suggest that significant corrections to standard fluid dynamic theory may be required when channel dimensions become small^{15,16,17}. There also have been observations of a quantized viscosity when the thickness of the fluid layers are of the order of 10 atoms thick ($\sim 2-3$ nm)¹⁸. Such thin layers may occur during multi-phase transport in low permeability porous media. However, the dimensions of the channels we will investigate are at least an order of magnitude larger than those studied by Israelachvili et al.¹³.

Figure 6: Schematic drawing of the flow structure under development

The major goals of our on going study are: (1) to determine if mesofluidic flow can be modeled by, or is fundamentally different from the corresponding macro-scale phenomena predicted by the Navier-Stokes equations; (2) to study the interaction of fluids with the walls, especially if the walls are chemically modified; (3) examining the influence of the liquid's molecular character on flow in micron and submicron channels; and (4) establishing the effect of surface asperities on fluid flow, especially those arising in the normal course of current micromachining processes. Preliminary results of this work are described below¹⁹. Experimental data are necessary since it is not known to what extent the continuum fluid mechanics laws are valid in the mesoscale regime. Current theory on flow in such small

channels assumes that continuum processes hold so long as the dimensions of the channel are more than an order of magnitude greater than the molecular dimensions. In large measure, this argument is due to the fact that characteristic lengths greater than the molecular size but less than the Kolmogoroff limit have not been observed in liquid flow. The types of structures being investigated in these studies offer the promise of establishing an experimental basis for testing current continuum mechanical fluid theory.

Because our experiments involve flow handling and measurement at low flow rates in very small channels, we are developing sensor capabilities to be integrated into the silicon flow cell "chip". Once this is accomplished, these micromachined structures will not only be well suited for scientific studies mentioned above, they also should provide valuable information on manu-

Figure 7: Exploded view of the modular fluid handling system

facturing and industrial flow processes involving small and complex structures [20].

In our present work on single phase fluid flow in micron and sub-micron size channels, silicon is the basic structural material used to manufacture the mesoscale flow structure. A recently developed prototype is sketched in Figure 6) and an exploded view of the modular fluid handling is depicted in Figure 7). In these early stages of our study, we have relied on a simple displacement of fluid in an external capillary as the means for measuring the fluid flow. The fluid from the flow cell is transported to the measurement capillary by a piece of tygon tubing and an adequate amount of time was required to insure that the flow conditions would reach a steady state value. In some cases, this was of the order of hours. The flow cell shown in Figure 6 is the latest version we are developing. The basic element containing the containing an integrated flow rate measurement structures has been completed and is in use now. Inclusion of the integrated pressure sensor and ion implanted electrodes is the next stage in the development of our measurement methodology.

The technology used to manufacture these flow cells is standard. The photolithographic masks for the devices have been designed and produced in our Microfabrication Facility. Both (100) and (110) oriented silicon wafers have been employed in the past to make the test sections using such standard photolithographic machining techniques as crystallographically selective wet (hot KOH solutions) and anisotropic dry (reactive ion) etching methods, depending on the depth of channels desired. The channel depth is obtained using an Alpha-step unit and its

uniformity over the 1 cm length of the channel is well within the 3-5% measurement uncertainty. After separation of the chips, the Pyrex cover plate is anodically bonded to the silicon chips at 300 V with a temperature of approximately 350-400°C. The resulting seal is hermetic and no leakage has been observed in any of the measurements conducted to date, even at pressures as high as 1.5 MPa. Channels as small as 65 nm have been made with this methodology but measurements have only been carried out on 480 nm or thicker channels. A description of the earlier devices used and some of the original results is in the literature¹⁷.

The current version of the flow cell, shown in Figure 6, has three entrance and exit holes (indicated as (1), (2) and (3)) to the other side of the chip. Two of these connect to the test channel, (1) and (2), while (2) and (3) connect to the flow monitor channel. The flow rate monitor channel is a larger cross sectional area channel that is partly filled with an immiscible fluid, e.g. mercury, that allows us to monitor the flow by observing the boundary motion. The flow cell is connected to a fluid handling system shown in exploded view in Figure 7. The fluid connections are made to the fluid access structures using liquid chromatography fixtures and piping.

The investigations into flow in these small channels has employed two liquids: propanol and a silicone oil (polydimethyl-siloxanetrimethylsiloxo terminated). The reason for choosing these two liquids

Figure 8: $C_{exp}/C_{theor.}$ vs. Re for propanol and a silicone oil.

was governed by the availability of extremely pure propanol in the laboratory and the fact that we had some corrosion problems with the fittings when deionized water was used in the preliminary studies. The according to the usual fluid dynamic theory, C also should be independent of Re . The ratio of the experimentally determined value, C_{exp} , to the theoretically determined value, $C_{theor.}$, for two (0.48 and 3.0 μm high) rectangular channels, 110 μm wide and 10⁴ micron long, is plotted as a function of the Reynolds number for n-propanol and a silicone oil in Fig. 8. Also shown is data for propanol flow through a 0.48 μm high channel with the same width and length. The values for the physical properties of the liquids employed in these studies are listed in Table II. Note that the bulk viscosity and specific gravity are reasonably similar. The major difference is in the molecular weight of the liquids. Further studies on other fluids are in progress which should clarify the generality of our

observations. These measurements include studies on gases.

TABLE II

Liquid	Type	Molecular Weight	Specific Gravity	Viscosity
n-propanol	Polar	60 Dalton	0.781	2.5 ctsk
Silicone oil (polydimethylsiloxane trimethylsiloxo terminated)	Non-polar	410 Dalton	0.873	2.0 ctsk

Earlier studies on larger channels (50 μm x 60 μm) demonstrated that good agreement could be obtained between the experimental and theoretical values for C^{17} . According to the Navier-Stokes equations with a no-slip boundary condition, C should be a constant with a value of approximately 94, assuming Newtonian behavior. For the alcohol, C is indeed a constant, though it is consistently lower than predicted over the range measured. Contrasting with this result, C for the silicone oil is clearly a function of the Reynolds number. Both fluids are known to exhibit Newtonian behavior in the range of strain rates encountered in these experiment. However, for high strain rates, silicone oils are known to exhibit shear thinning. Curiously enough, our experimental results instead suggest a "shear thickening"-like effect. We still feel it important to express caution about these very delicate measurements because of the extremely low flow rates encountered. We have remeasured the viscosity of the liquids used in these experiments to eliminate errors due to this source. While the thickness could be in error due to a systematic error in the Alpha step, we view this as unlikely. Further confirmation of these studies is clearly called for as well as a careful re-examination of the Navier-Stokes derivation of C . We can conclude that the causes of these anomalous results are as yet unknown.

DISCUSSION, FUTURE PLANS AND CONCLUSIONS

The results of the aforementioned study are not only important from a scientific point of view, they suggest some practical applications. The grating studies have revealed that there are

strong absorption processes associated with gratings of different dielectric character and dimension. Most important is that the electromagnetic energy can be concentrated in the grating region. This has been known before but what is new here is that spatially coherent surface modes of different wavelengths can be provide strong absorptions, especially in the conical diffraction direction. If inverse processes can be stimulated, i.e.

Figure 9: Depiction of possible EM Bloch states, depending on the carrier concentration of the grating solid. In the intermediate state, two degenerate states may exist.

photons can be absorbed strongly in these surface grating modes then it suggests the possible application of these structures to photochemical processes in the slots of the grating. An illustration of a possible electromagnetic Bloch wave is depicted in Figure 9 for three different solids. In the case of a dielectric the energy would be concentrated in the fins, i.e. solid. For a metal, the standing wave would be concentrated in the slot. For an intermediate carrier concentration, the energy will either be localized in both the fin and the slot or it will be "attached" to the walls of the fins as a surface mode. These two states are degenerate with regard to energy as shown here. However, no calculations or experiments have been conducted on this. An experiment is currently under way and results should be available shortly. If the energy can be shown to localize at the walls, it could lead to more efficient photochemical processes, especially those involving small quantities of materials. This controlled use of optical energy is one of the future directions of potential importance for improving the energy efficiency of photochemical processes.

A second interesting application is to excite impurity states in the surface region of a semiconductor. This area of application could lead to new classes of middle and far infrared photodetectors. Finally, combining the insights gained from the study of grating with the work on the fluid flow, creates the potential for new types of photochemical reactors. To further explore this subject it is important to obtain a more detailed understanding of the theory

associated with the vector interaction of electromagnetic radiation with deep partially conducting gratings. Further experimental efforts are needed on the propagation length of the surface grating modes.

Turning to the studies of flow in small channels, many processes in technology and nature involve fluid motion in minute capillaries, interconnected pores and cracks. Our observations to date (Fig.8) suggest that the rheological properties governing the transport of some liquids such as silicone oils in small channels may differ from their bulk properties. If true, this implies that contaminant transport in low permeability media may be at much higher rate than presently assumed. Our investigations indicate that photolithographic micromachining is an ideal means for generating well defined quasi-two dimensional flow structures for investigating a wide range of porous media. Such studies are of considerable direct importance for subsoil transport in dense matter. In addition, they offer an attractive way to examine various aspects of liquid-wall interactions and offer the prospect of developing new diagnostics for characterizing these interactions. There is a growing interest in hydrodynamic chromatography as a means for measuring the dimensions of large molecules and micelles by their delay when transported in solution through micron size capillaries. The small channels we have developed offer another route for investigating biochemical and biological molecules. Of interest to us is the possibility of gaining further insight into biological cell-wall interactions during cellular transport through our structures. Another direction is the use of these small channels as micro-chemical reactors, especially in conjunction with channels in the form of gratings. A final direction of interest is

the development of micron and submicron size multiple channels as micronozzles for chemical molecular beam epitaxy. This would be an extension of the current ink-jet application of small channels.

In conclusion, small structure provide an intriguing new class of elements whose interaction with energy and matter require additional study. The results obtained to date are sufficient to establish that as a scientific inquiry, the studies have promise. The added fillip of application to a wide range of contemporary issues makes this a particularly promising research area.

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