Brigham Young University
BYU ScholarsArchive

Faculty Publications

1992

Manufacturing of Atomically Sharp Silicon Tips and Their Use as Photocathodes

W. I. Karian
Brigham Young University - Provo, wqaran@birzeit.edu

Larry V. Knight
Brigham Young University - Provo, larry_knight@byu.edu

David D. Allred
Brigham Young University - Provo, allred@byu.edu

A. Reyes-Mena
Brigham Young University - Provo

Follow this and additional works at: https://scholarsarchive.byu.edu/facpub

Part of the Astrophysics and Astronomy Commons, and the Physics Commons

Original Publication Citation

W.I. Karain, Larry V. Knight, David D. Allred and A. Reyes-Mena, "Manufacturing of atomically sharp silicon tips and their use as photocathodes," Encyclia: The Journal of the Utah Academy of Sciences, Arts and Letters. 69, 257-272 (1992). [http://www.utahacademy.org/].

BYU ScholarsArchive Citation

Karian, W. I.; Knight, Larry V.; Allred, David D.; and Reyes-Mena, A., "Manufacturing of Atomically Sharp Silicon Tips and Their Use as Photocathodes" (1992). *Faculty Publications*. 1352.
https://scholarsarchive.byu.edu/facpub/1352

This Peer-Reviewed Article is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in Faculty Publications by an authorized administrator of BYU ScholarsArchive. For more information, please contact ellen_amatangelo@byu.edu.

MANUFACTURING OF ATOMICALLY SHARP SILICON TIPS AND THEIR USE AS PHOTOCATHODES

W. I. KARIAN, LARRY V. KNIGHT,
DAVID D. ALLRED, AND A. REYES-MENA*
Brigham Young University
*Also at Centro de Investigación y de Estudios Avanzados del Instituto Politecnico Nacional, México D.F., México

INTRODUCTION

The discovery and understanding of the photoelectric effect led to the study of photoemissive materials (Sommer, 1968). Practical photoemissive materials fall into two major categories: classical photoemitters and negative-electron-affinity (NEA) materials. Classical photoemitters usually involve an alkali metal, a group-V element such as phosphorus, silver, and/or oxygen. An example is the Ag–O–Cs (S1) photoemitter. NEA photocathodes consist of a photoconductive single crystal semiconductor covered with a thin layer of cesium and oxygen. This layer lowers the work function of the photocathode. A dipole layer is formed at the surface, and band bending occurs. This lowers the effective work function. An example is the GaAs(CsO) photocathode (Moore, Davis, and Caplan, 1989). Other photocathodes that are noteworthy include reverse biased p-n junctions, Schottky contacts, and metal-insulator-semiconductor structures (Miller and Jones, 1980). The electrons are formed as minority carriers in a p-type semiconductor and are then emitted over the metallic surface barrier that has been treated with cesium to lower its work function.

Unfortunately, all the above-listed photoemitters are sensitive to exposure to atmosphere. In the case of multialkali photocathodes, reaction with oxygen causes a considerable decrease in quantum efficiency (electrons emitted/incident photon) due to the reaction between its chemical constituents and oxygen (Sommer, 1968). Exposure to low vacuum also causes the migration of the thin layer of cesium from the surface of NEA photocathodes, causing a large decrease in the quantum efficiency of these cathodes (Lee et al., 1985). Also, exposure to unclean environments causes changes in the photoemitter work function due to adsorption of foreign material on the surface. This leads to an unstable performance by the photocathodes, requiring that they be kept and operated under very clean conditions and in ultra-high vacuum. This can be cumbersome, due to special cleaning procedures, and expensive, because of the ultra-high vacuum needed for continuous operation (Lee et al., 1985).

As alternative photoemissive materials, p-type semiconductors present characteristics that can help overcome the obstacles previously mentioned. The use of p-type semiconductors as photocathodes has been the object of research for many years (Thomas and Nathanson, 1972, 384–87). Recent developments in silicon technology have stirred considerable interest in this subject again (Turner, ed., 1989).

Semiconductors with low concentrations of conduction electrons show nonlinear field emission (that is, electrons tunneling through the surface to vacuum under the effect of a high electric field) characteristics (Baskin, Lvov, and Fursey, 1977). The emission is linear only at low applied fields. At higher fields, the emission is restricted by the arrival rate of electrons at the surface. Emission is thus source limited. The electron supply can be modulated by light and heat. Electrons can be excited from the valence band into the conduction band. This means that field emitters can be used as photocathodes and heat detectors in this nonlinear region of field emission (Thomas and Nathanson, 1972, 387–89). These photocathodes need no special surface treatments, which makes them an attractive alternative to more common photocathodes.

In this article we will describe the use of p-type silicon field emission arrays as practical photocathodes. We will outline problems encountered, as well as solutions. And we will point out potential applications.

QUALITATIVE THEORY

Field Emission from P-Type Semiconductors

In spite of a great deal of work, there is still not a complete theory for field emission from p-type semiconductors (Borzyak, Yatsenko, and Mirashnichenko, 1966). Field emission from p-semiconductors is more complex than field emission in metals for the following reasons:

a. emission is strongly influenced by the state of the surface
b. the electric field penetrates the semiconductor
c. the number of electrons in the conduction band is limited
d. emission can result from both the conduction and the valence bands. (Shroder et al., 1974)

Surface States

Chemically etched semiconductor surfaces form a thin oxide layer. Due to the mismatch between the crystallographic structure and the lattice constants at the oxide-semiconductor interface, the periodic structure is interrupted, leading to the creation of new energy levels in the forbidden gap. These extra energy levels are called surface states (Wang, 1989).

There are two types of surface states: donor and acceptor. Donor states can be neutral, or they can become positive by donating an electron. Acceptor states can be neutral, or they can become negative by accepting an electron. These surface states affect field emission from p-semiconductors. They act as generation sites of electron-hole pairs when the surface is depleted, similar to what happens when a p-n junction is exposed to light. Consider surface states that are neutral when occupied by holes. When the external field is applied to the field emitter, electrons are drawn to the surface, where some are captured by these surface states that become negatively charged. This allows them to act as field terminating charges, which shields the interior of the field emitter, thus lowering field penetration.

Field Penetration

If a conductor is placed in a static electric field, charge polarization occurs. This induces an internal electric field that will cancel the applied field inside the conductor and tangent to its surface. If a p-semiconductor is placed in the same electric field, the induced electric field inside will not be strong enough to cancel the applied

field, because of the lack of free electrons in the conduction band. Electric field penetration into the semiconductor results in

a. band bending, which changes the concentration of electrons at the surface from that in the bulk.
b. heating of current carriers, which changes the recombination conditions.
c. field ionization of impurity centers.
d. impact multiplication of carriers.
e. Zener band-band ionization.
f. anisotropy effects due to mechanical stress in the crystal. (Borzyak, Yatsenko, and Mirishnichenko, 1966)

Limited Electron Supply

P-semiconductors have a very small number of electrons in their conduction bands. The few present are due to impurities and thermal excitation. Due to this inherent deficiency, the number of electrons available for tunneling through the surface barrier is limited.

Emission from Valence Band

In very high electric fields exceeding 100 MV/cm, electron emission from the valence band of the semiconductor will dominate (Borzyak, Yatsenko, and Miroshnichenko, 1966). These added complications make it difficult to describe field emission from p-type semiconductors. However, a qualitative theory by Baskin, Lvov, and Fursey (1977) describes the main features of this phenomenon (see Figure 1). With the application of a strong electric field to the surface, a degenerate negative layer is formed there. This layer will screen the external field as long as small currents are being emitted. Thus emission is determined only by the tunneling probability at the surface. This is represented by region I in Figure 1. The semiconductor acts as a metal in this region, and the Fowler-Nordheim equation (Gomer, 1961) describes the emitted current well.

As the external field increases, the emission current should also increase. The electrons emitted will come from the negative surface layer. Consequently, this layer is weakened due to the limited supply of free electrons. This leads to an increased penetration by the field into the semiconductor. The surface of the sharp emitter is no longer an equipotential surface. Although the voltage applied between the emitter and the anode is increased, the electric field at the tip of

the sharp emitter is not increasing linearly with the voltage. This along with effects due to field penetration explain the saturation observed in region II of Figure 1.

If the applied voltage is increased further, the internal electric field is strong enough to cause impact ionization of electrons. This drastically increases the supply of free electrons available for emission. This is shown in region III in Figure 1. As the voltage increases further, the emission is again limited by the transparency of the surface barrier. There is an ample supply of electrons. The emission will again be well described by the Fowler-Nordheim equation. This is region IV of Figure 1.

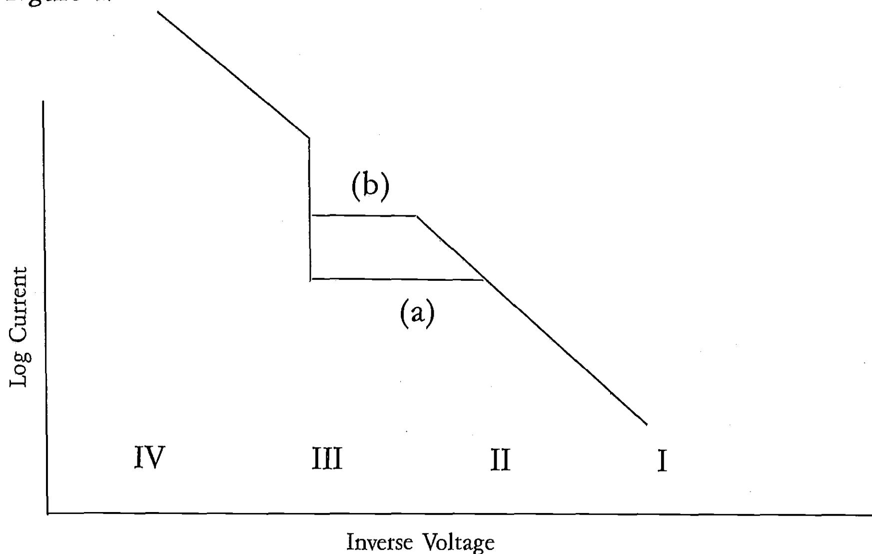


Figure 1
Field emission in p-type semiconductors.

MANUFACTURE

Oxidation

Semiconductors can be oxidized by thermal oxidation, electrochemical anodization or plasma reaction (Sze, 1985). For our silicon wafers, we used thermal oxidation. Thermal oxidation is a process in which silicon reacts with oxygen to form a continuous layer of silicon

dioxide (Maly, 1987). There are two types of thermal oxidation: wet and dry. Wet oxidation occurs when water vapor is allowed to react with silicon at temperatures between 900° C and 1100° C. Dry oxidation occurs when the silicon wafer reacts with dry oxygen at temperatures between 90° C and 1100° C. We used wet oxidation because it is faster. For a certain thickness of oxide to grow, the reaction time and temperature between the silicon and the water vapor must be known. Published curves can be used (Maly, 1987) to find these parameters.

Photolithography

Photolithography is the process of transferring patterns of geometric shapes, etched on a mask, to a thin layer of radiation-sensitive material (photoresist) covering the surface of a semiconductor wafer (Sze, 1985). The process of pattern transfer is accomplished with a lithographic exposure tool. There are two methods of optical exposure: shadow printing and projection printing. Shadow printing takes place when the wafer and the mask are making contact with each other (contact lithography) or when they are very close to each other (proximity printing). Projection printing is when the pattern is projected over a distance of several centimeters onto the surface of the wafer. The photoresist is spun on the wafers at high speeds to form a thin layer. The wafer is then placed in an oven at 90° C for 15 minutes. After the pattern is projected onto the photoresist-covered surface of the wafer for a certain amount of time, the photoresist is ready to be developed.

There are two types of photoresist (Sze, 1985): negative and positive. Positive photoresists consist of three components: a photosensitive compound, a base resin, and an organic solvent. Prior to exposure, the photosensitive compound is insoluble in the developer solution. During exposure, this compound absorbs radiation in the exposed pattern areas, changes its chemical structure, and becomes soluble in the developer solution. Upon development, the exposed areas are removed. Negative photoresists are polymers combined with a photosensitive compound. After exposure, the photosensitive compound absorbs the light energy, causing the polymers to become insoluble in the developer solution. Upon development, the unexposed areas are removed. We used positive photoresist. After the pattern is developed, the wafer is placed in an oven at 150° C. It serves to harden the photoresist left on the wafer to prepare for subsequent processing.

Etching

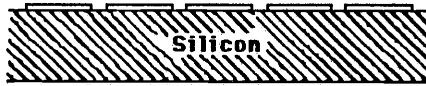
The process of etching follows the photolithographic processes previously mentioned. Etching is the removal of material on the wafer unprotected by hardened resist. Etching techniques are characterized by their selectivity (for example, attacking silicon dioxide and not silicon) and their degree of anisotropy (Maly, 1987). Anisotropic (preferential) etching occurs in one direction, while isotropic etching occurs equally in all directions. Two types of etching exist: wet and dry etching. In wet etching, the wafer is exposed to liquid chemicals. In dry etching, the wafer is exposed to gas under reduced pressure. We used wet etching. The standard etchant for silicon dioxide is buffered hydrofluoric acid. It consists of the following: 28ml HF, 170ml H_2O, 113g NH_4F. The etch rate is approximately 1000 Angstroms/min. There are many etchants for silicon (Bean, 1978). Some of these have etch rates that depend on the orientation of the wafer and are called orientation-dependent etches. Others will etch at the same rate in all directions and are called isotropic etches. We used the following isotropic etch: 3ml HF, 25ml HNO_3, 10ml CH_3COOH. The nitric and acetic acids oxidize the silicon and form silicon dioxide, which is then removed by the hydrofluoric acid. The observed etch rate was about 1 micron/min.

Making the Field Emitters

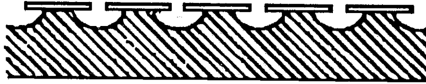
We adapted the following technique from Nathanson et al. (1974) to produce photosensitive field emitters from p-type silicon:

a. P-type silicon wafers with ‹111› orientation are used. One micron of oxide is grown on the wafer.
b. Positive photoresist is spun on the wafer at 9000 r.p.m. for 30 seconds.
c. The wafer is prebaked in an oven at 950° C for 20 minutes.
d. The wafer is then exposed. Proximity photolithography is used. The pattern to be transferred consists of squares with a certain feature size.
e. The photoresist is developed.
f. The wafer is postbaked at 150° C for 30 minutes.
g. The wafer is dipped in buffered hydrofluoric acid for 10 minutes. This removes the silicon dioxide not protected by hardened resist.
h. The wafer is dipped into resist stripper to remove the photoresist.

The wafer now has islands of oxide squares. It is dipped into the silicon isotropic etch mentioned earlier. This etch will attack the silicon, but not the oxide. Undercutting will occur, and sharp points will result (see Figure 2). This process is stopped when the silicon points are judged to be in the submicron region. This judgment is made by looking through the transparent oxide top with an optical microscope. The wafer is dipped into buffered hydrofluoric acid to remove the oxide squares. It is then placed in an oxidation reactor at 950° C for several hours. This oxidation step sharpens the silicon tips down to atomic dimensions (Marcus et al., 1990). The oxide formed is then etched away using buffered hydrofluoric acid. The wafer is then diced to facilitate testing.



1. 1 micron thick oxide pattern formed on silicon surface



2. etch silicon to undercut oxide discs

3. silicon etching continued until points formed oxide discs then removed in HF

Figure 2
Making sharp point field emitters (Thomas et al., 1974)

RESULTS AND DISCUSSION

Transferring the pattern from the mask is a crucial step. Slight differences in feature size are exaggerated during the etching process. We began with contact lithography. However, the contact between the wafer and the mask degraded the quality of the mask. We next tried proximity printing. When the pattern was transferred onto the wafer surface, the square sizes were not exactly the same. This led to uneven etching of the points (see Figure 3). Upon careful measurement of the mask, we found that the square size tolerance was too high. Consequently, a new mask with acceptable tolerance (0.25 microns) was made in chrome at a professional mask house.

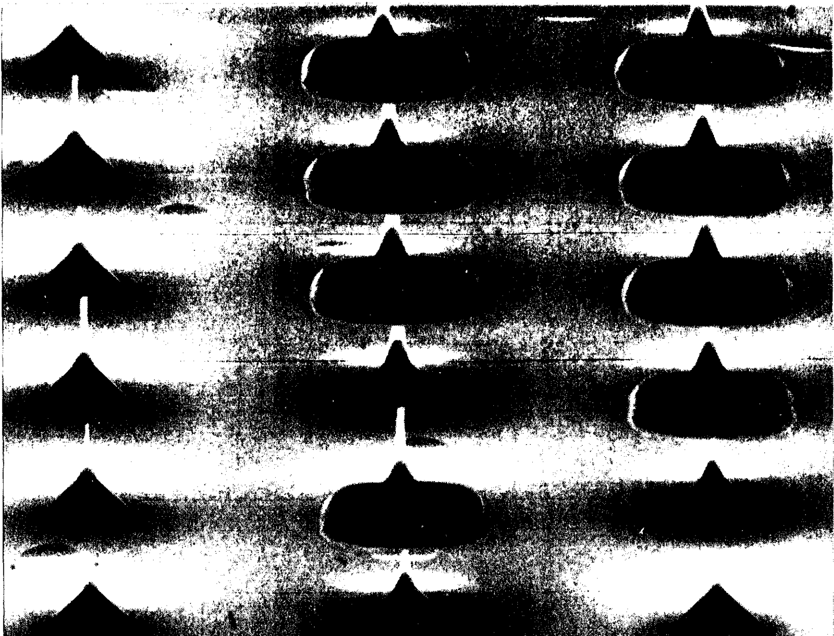


Figure 3
Uneven etching of points

For large areas of these field emitters to be obtained, a uniform etch rate is needed over the whole surface of the wafer. Simply placing the wafer in the isotropic silicon etchant with a magnetic stirrer resulted in nonuniform etching over the surface of the wafer. We tried a method that was used by Thomas et al. (1974) at Westinghouse. This consists

of placing the wafer in a beaker tilted at 45°. The beaker is rotated at a certain speed. By trial and error, a suitable speed can be found at which a uniform etch can occur over a significant area of the wafer (see Figure 4).

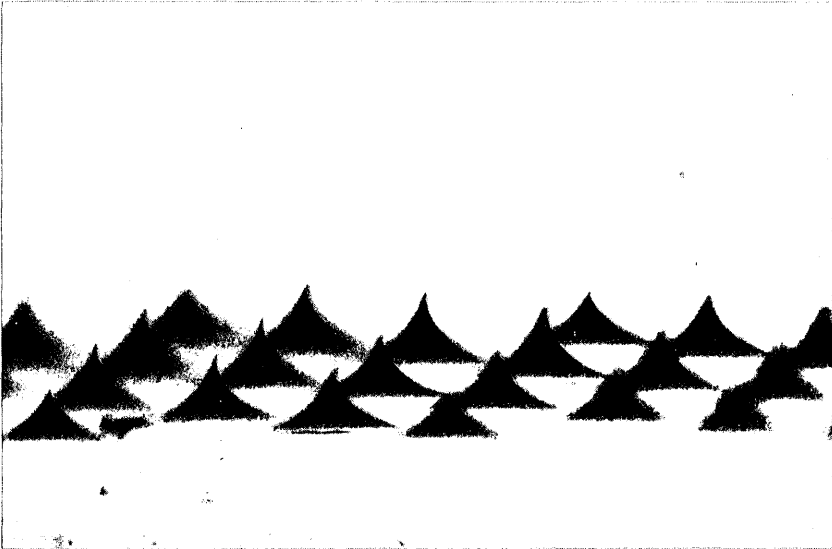


Figure 4
Array of uniformly etched points

The diameters of the sharp tips need to be as small as possible. As mentioned earlier, the etching is stopped when the points are judged to be in the submicron range by looking through the transparent oxide with an optical microscope. This introduces human error into the process. If etching is stopped too early, the points will not be sharp enough. On the other hand, if left too long, the points will be over-etched and equally useless. However, we did find a solution to this problem. After the etching is stopped, the wafer is oxidized at 950° C. A well-known phenomena (Marcus et al., 1990) of silicon is that oxidation of sharp points at temperatures lower than 1100° C will make them even sharper. Marcus et al. (1990) made silicon points less than 1nm thick using this method. Another feature of this phenomena is that the oxidation rate decreases asymptotically as the points get sharper. This means that even if points start with different tip thicknesses, they will end up with the same tip size. The heights

however will be different. This oxidation treatment can be repeated as many times as desired. The wafer is oxidized, the oxide layer is etched, and the process is repeated again and again (see Figure 5). Thus, this sharpens the tips and improves the tip thickness uniformity over the surface of the wafer.

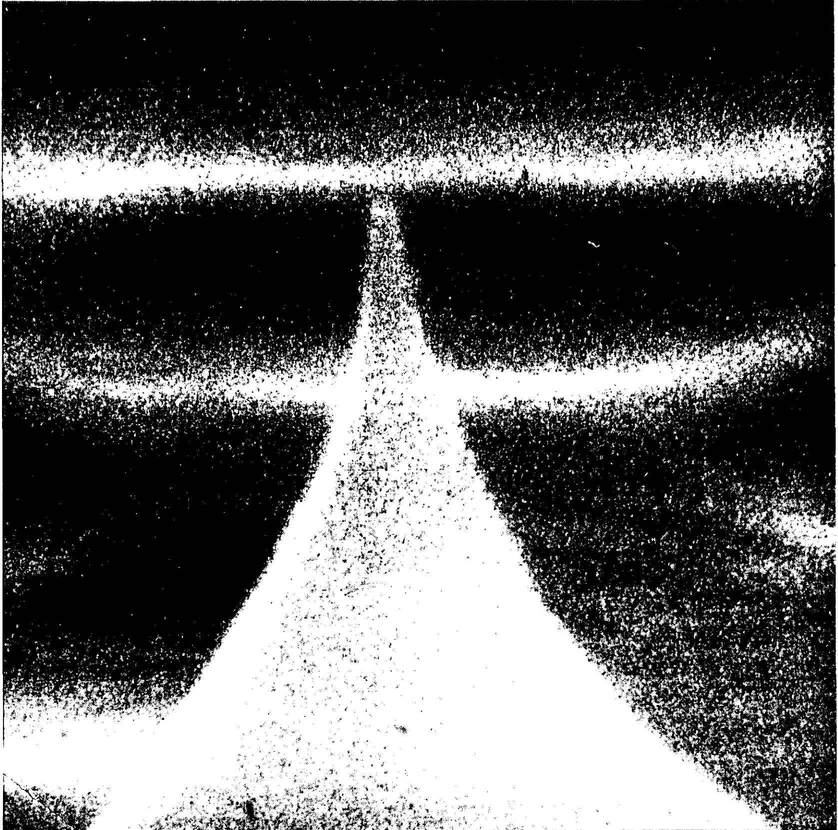


Figure 5
Sharp Point. The tip diameter is less than 30 nm.

Blunting of the tips can be a problem. This results from the heating of the tips if the emission current exceeds a critical value. This value depends on the tip surface roughness (see Figure 6) (Karain et al., 1993). The roughness is a function of the rate of ion bombardment of the tip. This can be minimized by using the tips in vacua of at least 10^{-8} Torr.

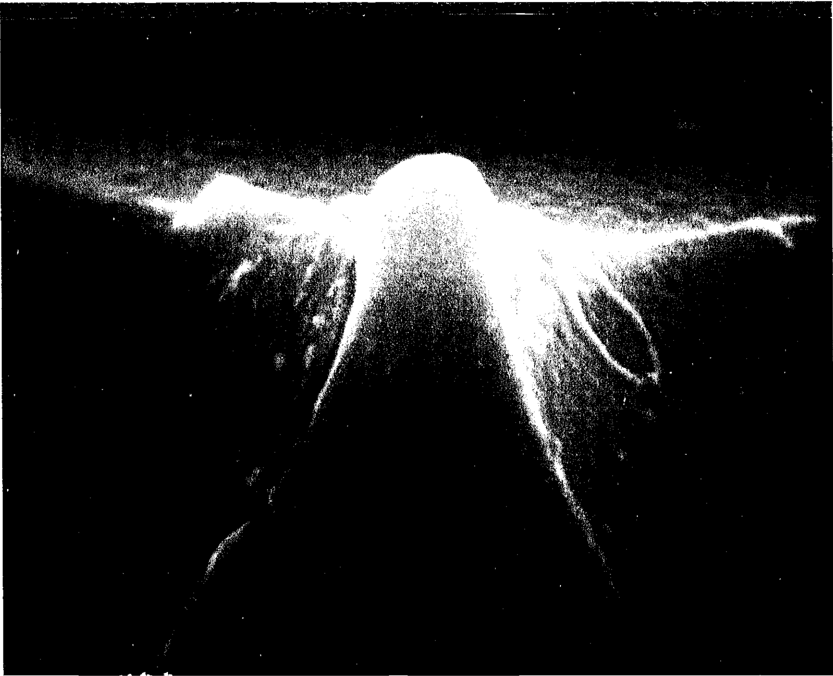


Figure 6
Damage. The sharp tip is blunted and will no longer emit electrons

Figure 7 shows current emission at room temperature for the array both in the dark (curve a) and under illumination (curve b). At low voltages (region I), the log of the emitted current is linear with the reciprocal voltage. The electron supply is adequate for the emission to be limited only by the barrier transparency. As the voltage increases, the current begins to saturate (region II). By illuminating the emitter array with a 5 mW, green He-Ne laser (543 nm), we were able to increase the emission current by as much as a factor of 4 (see Figure 7b). However, the laser showed no effect in region I. Currents with array under illumination were as high as 46 microamperes. This corresponds to a quantum efficiency of 0.02 at 543 nm. The photocurrent was roughly proportional to the power of light (Table I). This is expected because the supply function of electrons is being modulated by the laser. Keeping the voltage constant, we lowered the temperature of the emitters to 200K using a liquid nitrogen cold finger. This decreased the dark current by a factor of 10. When the

emitters were illuminated with laser light (543 nm) at this temperature, the current increased by as much as a factor of 8. This corresponds to a quantum efficiency of 2.6 X 10^{-3}.

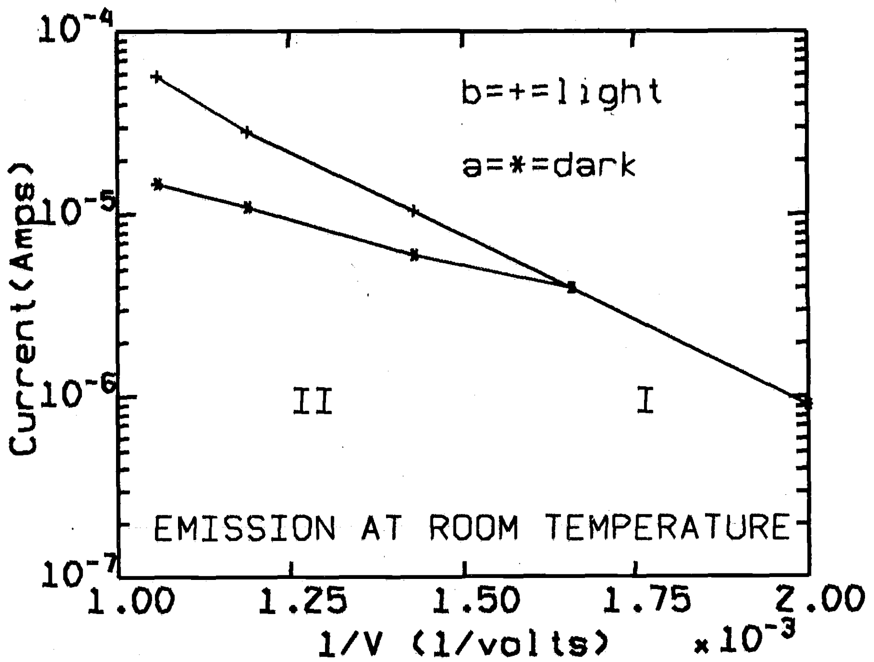


Figure 7
I–V characteristics of field emitters (experimental)

$P_0 = 5mW, P = power$

(P/P_0)	*photocurrent(P)*/photocurrent(P_0)
1	1
0.6	0.5
0.1	0.07
0.01	0

Table I. Photocurrent at various illumination powers (P) normalized to the photocurrent at 5 mW illumination. Note that the power ratios and the photocurrent ratios are roughly equal. These measurements were taken at 300K.

When the voltage is turned on, the dark current increases steadily for several minutes as it asymptotically reaches a steady value for a given voltage. This has been attributed to some form of cleaning by the bombarding ions in the cavity between the photocathode and the anode (Thomas et al., 1974). The photocathode was cycle tested. Between testing cycles, it was kept in static vacuum. The initial, gradual increase in the current as the voltage is first applied was observed in all cycles. Emission was stable for several hours. However, the emission current continued to increase steadily with each cycle. A possible explanation could be the increased surface roughness due to ion bombardment, leading to a localized increase in the electric field at the tip, which increases the emitted current.

APPLICATIONS

Arrays of atomically sharp silicon tips can serve as photocathodes. Their main advantages over conventional cathodes is the ease with which they can be manufactured and their resistance to contamination upon exposure to the atmosphere. This can be very important in that it offers the user more flexibility in using the photocathode without having to worry about storing the cathode in ultrahigh vacuum when not in use.

Due to the small bandgap of silicon, this photocathode can be used in the infrared red wavelength range. This can lead to applications in infrared and night imaging. In addition, the measured electron currents are large enough for this photocathode to be used as an electron source for a soft x-ray source. This small, compact source would be valuable in a variety of potential applications, such as x-ray imaging and analytical instruments. It would be a high brightness source due to the small spot size of the electron emitters. The emission can also be modulated temporally and spatially by modulating the light signal incident on the photocathode.

CONCLUSIONS

Proximity printing was used to produce the lithographic pattern with a feature size of 25 microns and a tolerance less than 0.25 microns. This was followed by a rotational etching technique to obtain the preliminary silicon tips. The subsequent oxidation treatments at 950^{0} C

led to atomically sharp silicon tips. Tip thickness uniformity has also been achieved over significant areas exceeding several mm^2. The exact number of emitting tips is unknown. However, some samples show yields higher than 50 percent, judging from scanning electron microscope inspection. Electron emission currents of several microamperes were measured. Photosensitive electron emission was also detected at room temperature and at liquid nitrogen temperature. Emission quantum efficiencies of 0.02 were measured at 543 nm. Stable electron emission was also measured over several hours of cycle testing.

REFERENCES

Baskin, L. M., O. I. Lvov, and G. N. Fursey. ''On the Theory of Field Emission from p-type Semiconductors.'' *Physica Status Solidi, 42,* 757–767 (1977).

Bean, Kenneth E. ''Anistropic Etching of Silicon.'' *IEEE Transactions on Electron Devices.* Vol. ED–25, 1185–1193 (1978).

Borzyak, P. G., A. F. Yatsenko, and L. S. Miroshnichenko. ''Photofield Emission from High Resistance Silicon and Germanium.'' *Physica Status Solidi, 14,* 403–411 (1966).

Gomer, Robert. *Field Emission and Field Ionization.* Cambridge: Harvard University Press, 1961. Chapter 1.

Karain, W. I., Larry V. Knight, David D. Allred, and Arturo Reyes-Mena. *Journal of Nanostructure Materials* (1993).

Lee, Chunghsin, Peter E. Oettinger, Alan Sliski, and Marvin Fishbein. ''Practical Laser-activated Photoemissive Electron Source.'' *Review of Scientific Instruments, 56,* 560–562 (1985).

Maly, W. *Atlas of IC Technologies.* Menlo Park, Calif.: Benjamin/Cummings Publishing Company, 1987.

Marchus, R. B., T. S. Ravi, T. Gmitter, K. Chin, D. Liu, W. J. Orvis, D. R. Ciarlo, C. E. Hunt, and J. Trujillo. ''Formation of Silicon Tips with <1 nm Radius. *Applied Physics Letters, 56,* 236 (1990).

Miller, Brian S., and Terry L. Jones. ''A Metal/insulator/semiconductor (MIS) Photocathode.'' *IEEE Transaction on Electron Devices.* Vol. ED–27, 2089–2096 (1980).

Moore, John H., Christopher C. Davis, Michael A. Coplan. *Building Scientific Apparatus: A Practical Guide to Design and Construction.* Redwood City, Calif.: Addison-Wesley, 1989.

Schroder, Dieter K., R. Noel Thomas, James Vine, and H. C. Nathanson. ''The Semiconductor Field Emission Photocathode.'' *IEEE Transaction on Electron Devices,* Vol. ED–21, 785–798 (1974).

Sommer, A. H. *Photoemissive Materials: Preparation, Properties, and Uses.* New York: Wiley, 1968.

Sze, S. M. *Semiconductor Devices, Physics and Technology*. New York: Wiley, 1985.

Thomas, R. N., and H. C. Nathanson. "Photosensitive Field Emission from Silicon Point Arrays." *Applied Physics Letters, 21,* 384–387 (1972).

Thomas, R. N., and H. C. Nathanson. "Transmissive-mode Silicon Field Emission Array Photoemitter." *Applied Physics Letters, 21,* 387–389 (1972).

Thomas, R. N., R. A. Wickstrom, D. K. Schroder, and H. C. Nathanson. "Fabrication and Some Applications of Large-Area Silicon Field Emission Arrays." *Solid State Electronics, 17,* 155–163 (1974).

Vacuum Microelectronics, 1989. R. E. Turner, Ed. Institute of Physics Conference Series, No. 99. Bristol, England: Institute of Physics, 1989.

Wang, Shyh. *Fundamentals of Semiconductor Theory and Device Physics*. Englewood Cliffs, N.J.: Prentice Hall, 1989.

ACKNOWLEDGMENTS

We would like to acknowledge the valuable help of Dr. Richard Woodbury, Dr. Linton Salmon, and Tony Fucile in making the tips. We would also like to thank Dr. John Gardner and Mike Standing for their assistance with the scanning electron microscope measurements. Also, special thanks to Merrill Olsen and Signetics Orem for their help in dicing the wafers and Wes Lifferth for his help with machining the measurement device.