

# Exhibit A



Page [ ] of [ ] pages  
of DESCRIPTION  
(copy form as needed)

PATENT CAUTION

This document may reveal patentable matter and must not be divulged outside Sandia National Laboratories without the approval of the Patent and Licensing Office. Approved external recipients must not divulge the information to others.

DESCRIPTION

I have attached a copy of the 16-page *Disclosure and Record of Invention* filed and witnessed at the University of New Mexico.

-Bruce Draper

SIGNATURES

Originator _____	Date _____	Originator _____	Date _____
Originator _____	Date _____	Originator _____	Date _____
Originator _____	Date _____	Originator _____	Date _____

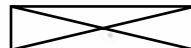
We have read and understood the foregoing description

Witness

Date

Witness

Date





THE UNIVERSITY OF NEW MEXICO  
DISCLOSURE AND RECORD OF INVENTION

UNM Docket UNM-847  
Admin. Confidential

INSTRUCTIONS: This is a legal document and its careful preparation is very important. See back for guidance.

**A. Each Inventor's Name, Address, and Name of Employer:**

S.R.J. Brueck - UNM Cntr for High Tech Mat/5601 Cometa Ct. N.E.  
An-Shang Chu - UNM Cntr for High Tech Mat/ 1420 Monzano St. N.E.  
Saleem Zaidi - UNM Cntr for High Tech Mat/5360 San Mateo, #4 N.E.  
Bruce L. Draper - Sandia National Lab.

**B. Invention Title:**

Method for Fabrication of Quantum Wires and Quantum Dots and Arrays of Same

**C. Invention History:**

1. Date conceived June 4, 1991 at (place) Albuquerque, NM
2. Date first shown to work successfully Sep. 10, 1991 at Albuquerque, NM
3. Sponsor's contract, grant or agreement number under which invention arose, and name of sponsor. If none, write "none".  
AFOSR Contract #F49620-89-C-0028

4. Names of 2 witnesses (not coinventors) who, by their signatures below, attest that the invention was disclosed to and understood by them.

a. Kevin J. Malloy 3 Sept 92  
Signature and date

b. Anadi Mukherjee 4 Sept 92  
Signature and date

Print names and addresses of witnesses:

a. Kevin J. Malloy  
7229 General Kearny Ct. NE  
Albuquerque, NM 87109-6304

b. ANADI MUKHERJEE  
1423 MADISON NE  
ALBU, NM 87110

**D. Initial Invention Protection/Use Factors:**

1. Publication date, if any \_\_\_\_\_ in (journal, etc.) \_\_\_\_\_  
Intended future publication date \_\_\_\_\_ in \_\_\_\_\_
2. Past date \_\_\_\_\_ or future date September 20, 1992  
of X oral or \_\_\_\_\_ written presentation at symposium, conference, classroom etc (Attach copy of item divulged or to be divulged)
3. Date invention was sold \_\_\_\_\_ or placed on sale \_\_\_\_\_  
or publicly used \_\_\_\_\_ or, if none of the above write "none" \_\_\_\_\_
4. Inventor(s) opinion on commercial uses of invention attached

**E. Brief Description of Invention** (Attach pages containing description and sketches.) attached

**F. Identify Prior Publications or patents which may constitute prior art:** \_\_\_\_\_

**G. Inventor(s) acknowledge that under UNM patent policy UNM owns the invention and inventor(s) are entitled to a share of royalties. Inventor(s) agree to timely execute all papers and assignments relating to protecting and licensing the invention.**

S.R.J. Brueck 9/3/92  
First inventor/signature and date

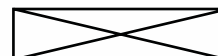
An-Shang Chu 9/3/92  
Second inventor/signature and date

Saleem Zaidi 9/3/92  
Third inventor/signature and date

Bruce L. Draper 6/28/93  
Fourth inventor/signature and date

\_\_\_\_\_  
Fifth inventor/signature and date

\_\_\_\_\_  
Sixth inventor/signature and date



# METHOD FOR FABRICATION OF QUANTUM WIRES AND QUANTUM DOTS AND ARRAYS OF SAME

## Inventors:

S. R. J. Brueck, An-Shiang Chu and Saleem H. Zaidi, University of New Mexico and Bruce L. Draper, Sandia National Laboratories all of Albuquerque, NM

Support: Support for the UNM portion of this work was provided by the Air Force Office of Scientific Research, support for the SNL portion (?)

## Background of the Invention:

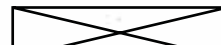
Semiconductor quantum structures are physical structures with dimensions on the order of electronic wavefunctions. The most familiar examples are the quantum wells common in semiconductor laser structures. For example, a thin GaAs layer sandwiched between two larger bandgap AlGaAs layers. As a result of the band offsets characteristic of these two materials, both electrons and holes are confined to the thin GaAs layer. As the thickness of this layer is reduced to less than the de-Broglie wavelength of the electron, on the order of 30 nm, the electronic wavefunctions are modified. This is manifest both by increases in the electronic energy levels and a change in the electronic density-of-states with a significant increase in the density-of-states at the bottoms of the conduction and valence bands. These increases in the density-of-states are a major reason for the advantages of quantum wells over bulk material in laser structures. For example, because of both spatial and momentum localization of the carriers, a lower pumping density is required to achieve gain and lasing threshold in a quantum well structure than in a bulk material.

Quantum wires and quantum boxes are the two and three dimensional analogs of quantum wells, respectively. There are further increases in the band edge densities of states that accompany each increase in quantum dimensionality. For quantum boxes, in fact, there is no longer a band; in a naive sense, a quantum box is a man-made atom! Because of both the intrinsic interest in quantum phenomena and of the technological advantages, there have been significant efforts at achieving quantum structures and devices such as lasers based on the properties of these structures. While it is possible to form sufficiently small structures in GaAs and other III-V materials by various processing techniques, usually initiated with high resolution lithographies such as e-beam and focused ion-beam, these efforts have been hindered by the poor qualities of the III-V interfaces with other materials (vacuum, SiO<sub>2</sub>, etc.). In addition, these lithographies are better suited to one-of-a-kind structures than to large-scale high yield manufacturing. This approach is thus more suited to laboratory

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investigations available to only a very limited number of investigators with the necessary (and expensive) equipment. Another approach has been to take advantage of the crystallographically dependent growth properties that form when growing on patterned structures (V-grooves, mesas, etc.) in appropriate growth regimes. Under the right growth conditions, narrow quantum wire structures will form at edges (bottom of the V-groove, corner of a mesa, etc.). Here, it is difficult to control the dimensions of the quantum structures to be sufficiently small; the growth often occurs on relatively poor quality material (i. e. there are more imperfections at edges); and it is difficult to fabricate dense arrays of uniform quantum structures. Largely for these reasons, the demonstration of quantum wire lasers remains a tour-de-force experiment rather than a repeatable manufacturable process.

Recently, there has been much interest in the properties of quantum structures in Si following the observation of efficient, visible wavelength photoemission from porous Si materials. Si has an indirect bandgap and, in general, has weaker interactions with electromagnetic fields than do III-V compounds. The mechanism for this emission is still under investigation with two major theories being proposed: 1) quantum structure effects due to the very small,  $< 50$  nm, wire like structures found in porous Si, and 2) surface effects due to loss of crystal structure and chemical bonding (variously determined to be  $\text{SiH}_2$  and  $\text{SiOH}$  species) at the porous Si surface. There have also been observations of electroemission, particularly during electrochemical reactions forming the porous Si. Because of the pervasive presence of Si in microelectronics, there has been much interest in pursuing a Si-based alternative to optical emission (light-emitting diode) and perhaps to lasing. Accomplishment of these goals might reduce the need for hybrid approaches to optical interconnections and other applications that bring together both optoelectronics and microelectronics. It is widely thought that optical interconnections within high performance computers will be a relatively near-term application of optoelectronics. The availability of Si-based optical sources would make this a much more attractive alternative.

#### Brief Description of the Invention:

Using a simple interferometric technique, dubbed fine-line interferometric lithography, we have demonstrated the fabrication of uniform arrays of quantum-wire structures in both Si and III-V semiconductor materials. This technique is the subject of a related invention disclosure. We have taken advantage of nonlinearities in the exposure, develop and etch processes to make a periodic grating structure with very narrow lines, much smaller than the limit imposed by the linear variation of the aerial image of the optical intensity on the photoresist ( $\sim \lambda/4$  where  $\lambda$  is the optical wavelength). Further, we have taken advantage of the highly anisotropic

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03 Sept 92



etching of  $\langle 110 \rangle$  Si to fabricate structures with very high aspect ratios (to over 100:1 depth/width) and nearly atomically smooth sidewalls.

Using multiple exposures (also disclosed in the related invention), arrays of quantum-wire-like structures may be connected to buss-bars that run perpendicular to the wires. This will enable injection of carriers similar to that practiced in conventional laser and light-emitting diode structures. Finally, using the property that Si oxidation rates are inversely related to the local Si curvature we have demonstrated that Si quantum wires, passivated with  $\text{SiO}_2$  all about the circumference can be fabricated. The Si- $\text{SiO}_2$  interface has a much lower recombination velocity than do (III-V)- $\text{SiO}_2$  interfaces and should allow fabrication of useful device structures.

Figure 1 shows the fabrication sequence used to make very thin (to 30 nm or thinner) Si structures on  $\langle 110 \rangle$  oriented substrates. In the first step a thin  $\text{Si}_3\text{N}_4$  (50 nm) layer is deposited by any of a variety of well-known processes (LPCVD, PECVD,...). The purpose of this nitride layer is to serve as an etch mask for later process steps. A thin photoresist layer (150-200 nm) is then deposited on top of the photoresist. This photosensitive layer is then exposed using the fine-line interferometric lithography technique in which the exposure dose is optimized to achieve the smallest dimension of unexposed resist. If the KOH etching process described below is to be used, care is taken to align the grating grooves along the  $\langle 110 \rangle$  crystal directions. A develop process is then employed to remove the exposed photoresist. Again, this process is optimized to yield narrow linewidths. Linewidths of 100 nm or less are readily achievable in this way. A plasma etch process ( $\text{CF}_4$  etchant) is then used to etch through the  $\text{Si}_3\text{N}_4$  layer. This can be somewhat overetched to further narrow the lines. The F radicals that result from the plasma discharge in  $\text{CF}_4$  are an isotropic etchant and will attack the Si under the nitride mask layers as well as the bare Si in the exposed areas. This can be used as a further nonlinear step to narrow the lines. The photoresist, which serves as the etch mask during this first etch process is then removed leaving a  $\text{Si}_3\text{N}_4$  mask for the following steps. For the finest lines, a KOH wet etch step follows. KOH is a highly anisotropic etchant which leaves the  $\langle 111 \rangle$  Si faces almost totally unetched while rapidly etching the  $\langle 110 \rangle$  and  $\langle 100 \rangle$  and other crystallographic directions. The strong selectivity ( $\sim 400:1$ ) leads to very high-aspect ratio (as much as 50:1 or higher) very narrow Si walls. These are illustrated in figure 2 which is a scanning electron micrograph (SEM) of 40-nm wide, 2- $\mu\text{m}$  deep, Si walls on a 340-nm pitch. The sidewalls of these structures are  $\langle 111 \rangle$  crystal faces and are perpendicular to the top  $\langle 110 \rangle$  orientation. Due to the high anisotropy of the etching process, imperfections in the in the photoresist profile due to molecular inhomogeneities, optical artifacts, inhomogeneous development etc. are dramatically reduced in this step. Indeed, the dark lines on the

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sidewalls running off at an angle to the vertical are steps corresponding to another low etch rate crystalline direction. Finally, the silicon nitride cap layer can be simply etched off with diluted HF to leave an all Si structure. These structures are similar to quantum wells in that they have one dimension on the order of carrier wavefunctions. Most often quantum wells have been fabricated by epitaxial growth; this technique provides a new method of producing quantum size structures in Si materials. Epitaxial growths are limited by the growth process to total thickness on the order of 10  $\mu\text{m}$ . With the present technique we are limited only by the laser spot dimensions which can be as large as 10x10  $\text{cm}^2$  or larger. Thus, much larger arrays of quantum structures can be fabricated by this technique than can be accessed by traditional growth techniques.

The use of multiple exposures to form more complex arrays of quantum structures is illustrated in figure 3. This shows an array of 50-nm wide Si quantum wells on a 0.5  $\mu\text{m}$  pitch. The double exposure moiré pattern evident in the top view of the structure (right) was obtained with the very slight rotation of 1.2° between exposures. This results in the ~ 1- $\mu\text{m}$  wide "buss-bars" running perpendicular to the quantum structures spaced every 12  $\mu\text{m}$ . These "buss-bars" provide a convenient means of electrically contacting the quantum structures, a requirement for electrical excitation. It is possible, using well-known techniques, to provide a transverse p-n junction, before fabrication, in the region between the buss-bars. This would allow carrier injection in the region of the quantum wires with the upper and lower "buss-bars" alternately doped p and n type.

A further extension of these structures to quantum wires can be achieved by a thermal oxidation step. Figure 4 shows a SEM of an array of Si structures similar to the quantum wells described earlier but somewhat wider than quantum dimensions (150 nm). Figure 5 shows the results of a thermal oxidation of these structures with an oxidation thickness of ~ 70 nm from each side. The remaining Si is the darker material in the center of each structure, as well as across the entire bottom of the material. The Si may be more easily visualized after an HF etch step to remove the  $\text{SiO}_2$  formed during the oxidation. This is illustrated in the SEM of figure 6 which shows the resulting Si structure. Note that the Si "fingers" are somewhat concave. This is the result of the local curvature dependence of the oxidation rate. Si thermal oxidation is faster on plane surfaces than it is on sharply curved surfaces. This effect has been used previously to sharpen Si tips for scanning force microscopy and field-emitter tip applications. If the oxidation leading to figure 5 is further extended, the middle region of the Si is pinched off by the oxide and a single-crystal Si quantum wire is formed in the upper region. This is illustrated in the SEM of figure 7 which shows the quantum wires as the slightly darker ellipses with dimensions of ~ 20x30 nm in the upper

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center of the oxide. Note that these quantum wires are formed of single crystal Si which can be doped by any of a number of well-known techniques prior to this fabrication. The quantum wire is completely surrounded by a thermal oxide which provides a superior passivation and isolation from the surroundings. The multiple exposure techniques provide means for electrical connection to arrays of these quantum wires. Similar techniques are possible for quantum boxes. For example isolated posts may be fabricated by a multiple exposure technique as illustrated in the example of figure 8. Oxidation of these structures will result in a two-dimensional array of Si quantum boxes, again passivated by oxide films.

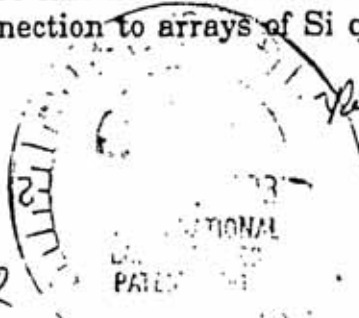
A further refinement of these ideas is the string of "quantum structures illustrated in figure 9. Using a multiple exposure technique similar to that used for a two-dimensional array of quantum dots but adjusting the exposure level such that these dots are not completely isolated, we will be able to gain some of the advantages of the reduced dimensionality over quantum wires but still retain the capability of electrical excitation.

#### BASIS FOR CLAIMS:

- Optimization of fine-line interferometric lithography for very small structures of order 50 nm or less. This is much smaller than the commonly assumed wavelength limitations and is accomplished by exploiting nonlinearities in the photoresist exposure and develop steps.
- Fabrication of very high aspect ratio, quantum-dimensioned walls in Si using combination of fine-line interferometric lithography optimized for small dimensions and highly anisotropic KOH etching of Si. Further nonlinearities can be exploited in this step for additional reduction in the dimensions.
- Fabrication of quantum size structures and arrays in III-V compounds using reactive-ion etching or ion-beam milling or other well-known means of anisotropic etching following optimization of the fine-line interferometric lithography.
- Fabrication of quantum-wires in Si, using combination of fine-line interferometric lithography optimized for small dimensions, highly anisotropic KOH etching of Si and local curvature dependent thermal oxidation.
- Use of multiple exposure fine-line interferometric lithography to provide means of electrical connection to arrays of Si quantum wires formed by above process.

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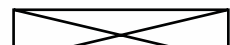
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- Use of known doping techniques to provide p-n junctions along the length of quantum wires formed by above process.
- Use of multiple exposure fine-line interferometric lithography coupled with anisotropic etching and Si thermal oxidation to provide strings of quantum dots connected by thinner quantum wires: "quantum pearls."

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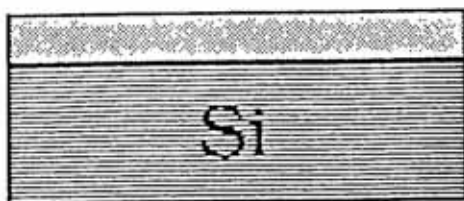
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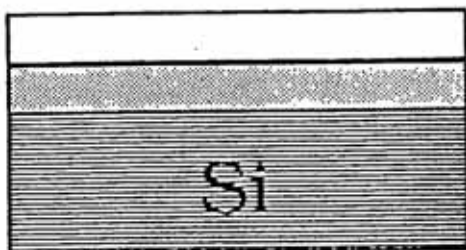


# Fine Line Lithography

deposit  $\text{Si}_3\text{N}_4$



deposit P.R.



exposure



develop P.R.



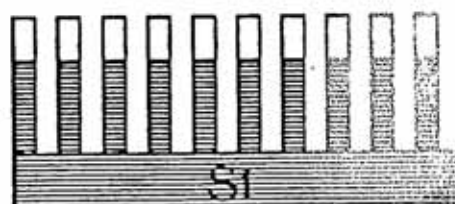
plasma etch



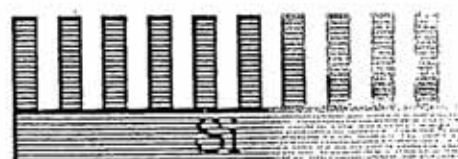
remove P.R.



wet or dry etching



remove  $\text{Si}_3\text{N}_4$



ad  
ford

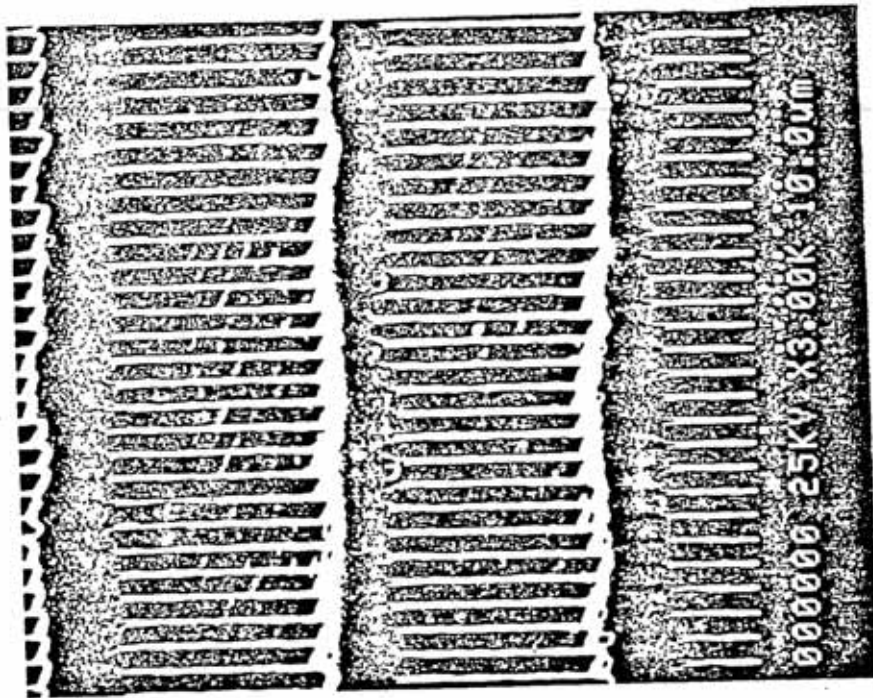
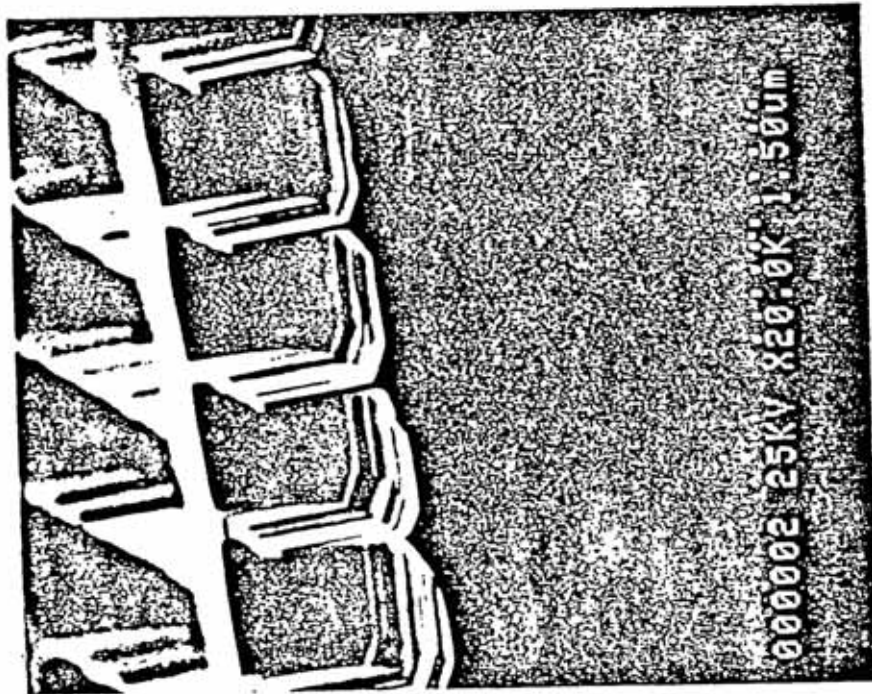
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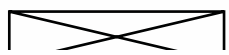


MOIRÉ STRUCTURES IN Si

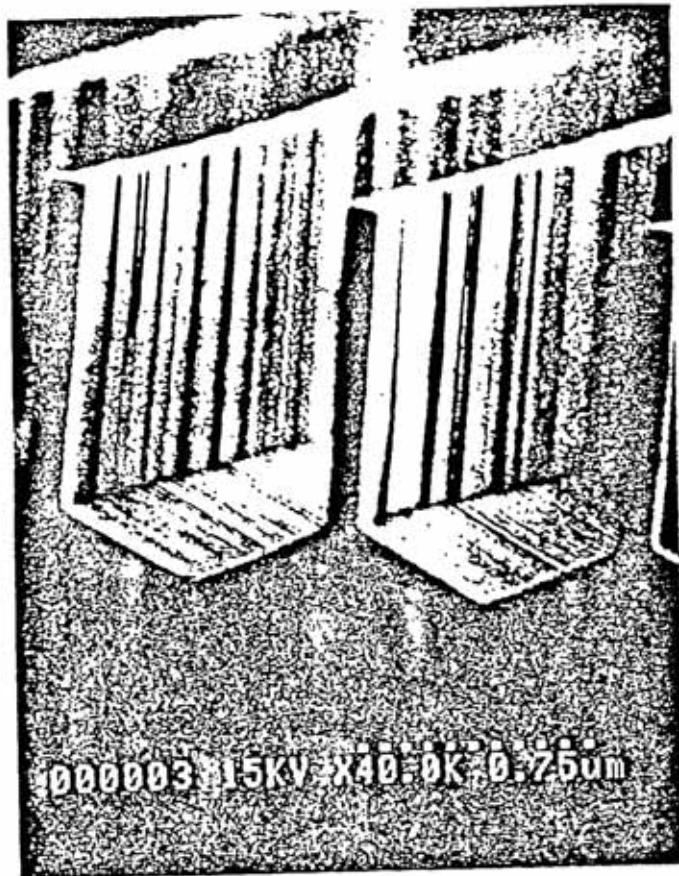


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 Anadi Mukherjee.  
 9-4-92

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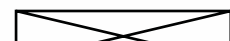


#7 8/27/91 Si<110>

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 Qasbi Mukhtaf  
 9-9-92

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 Ken! M. Allen

Fig. 4



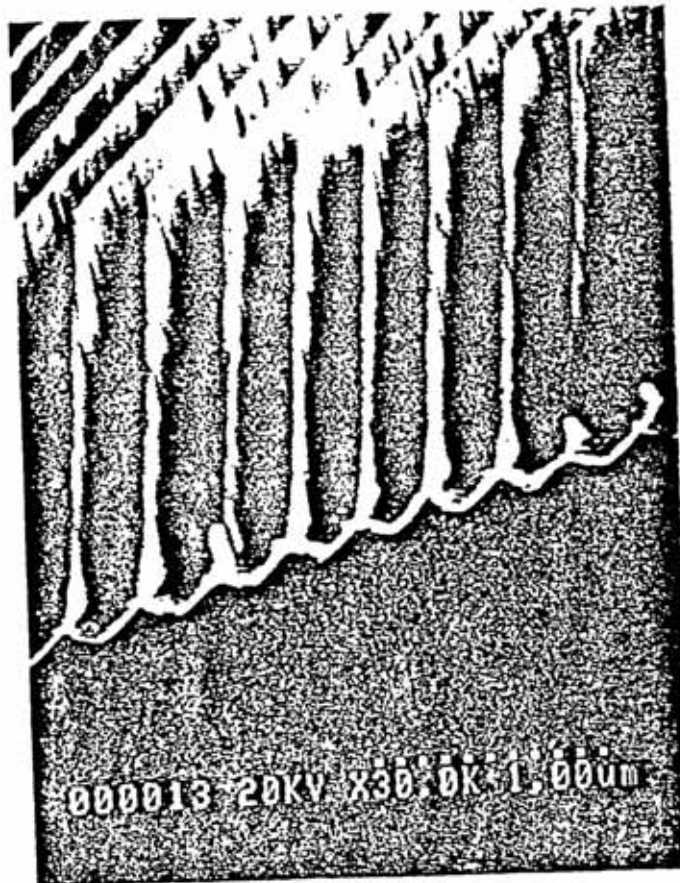
# HIGH-ASPECT RATIO STRUCTURE IN Si

Period = 340 nm

Line width = 40 nm

Depth = 2000 nm

Aspect-ratio = 50



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**original linewidth:  $0.15\mu\text{m}$**   
**oxidation depth~  $0.06\mu\text{m}$**

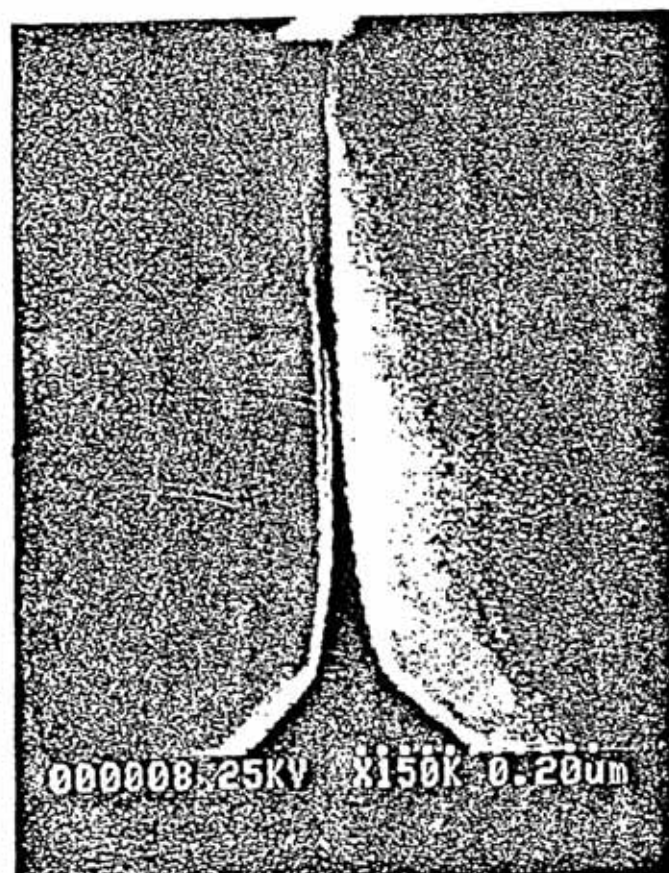
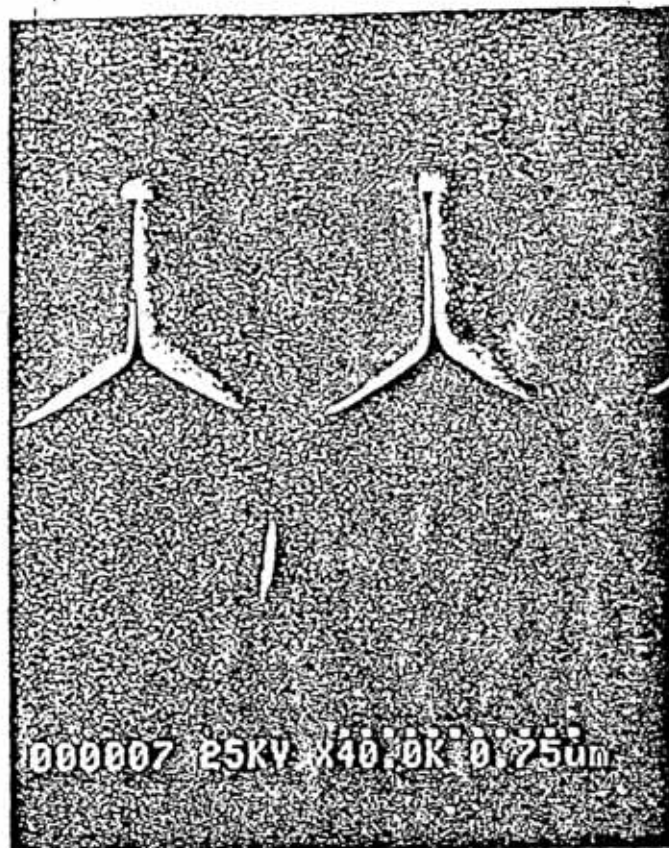
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3 Sept 92

Fig 5







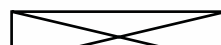
period: 1.0 $\mu$ m height: 0.5 $\mu$ m linewidth~ 100 $\text{\AA}$

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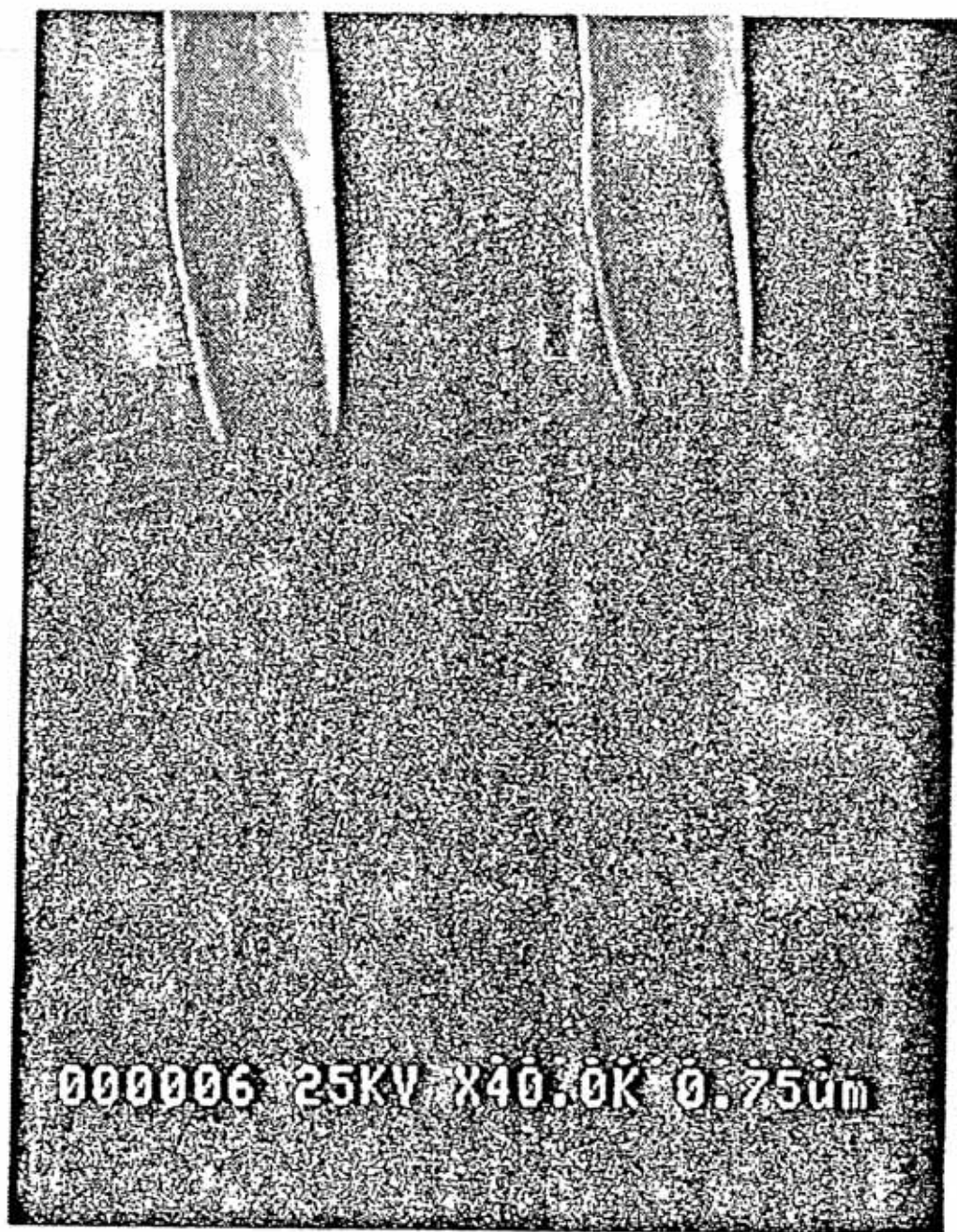
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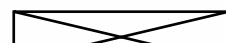




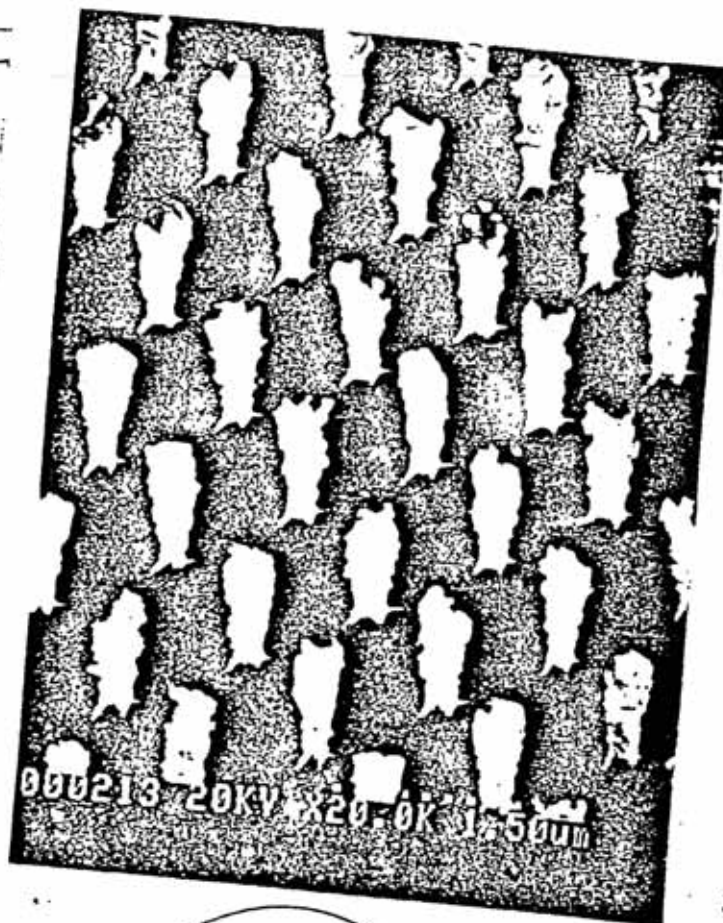
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Fig 7

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Kef Malby







gra

Fig 8

gave to Rf



RZE

6/27/90(6)

1/20um

1350 p.e.

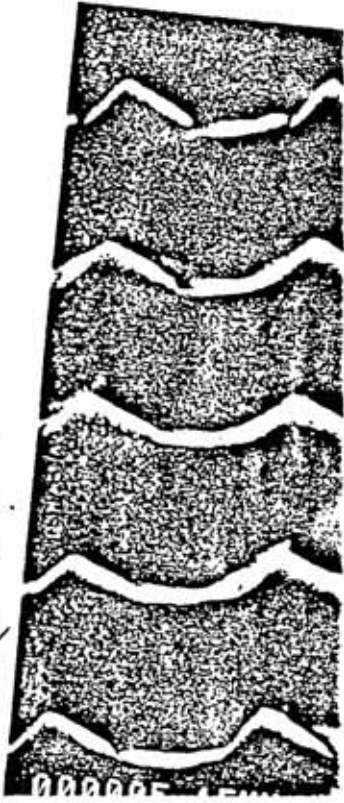
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Exposure in two dimensions

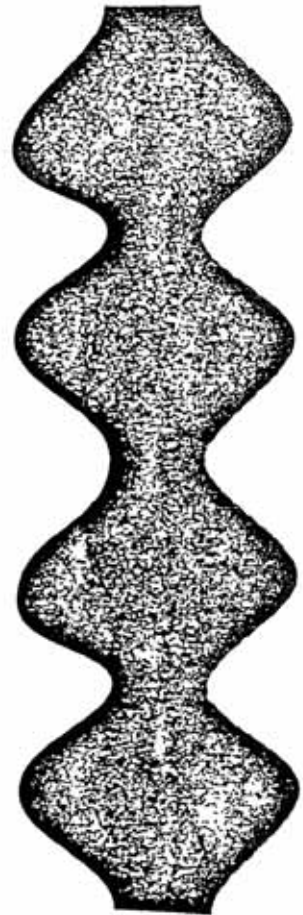
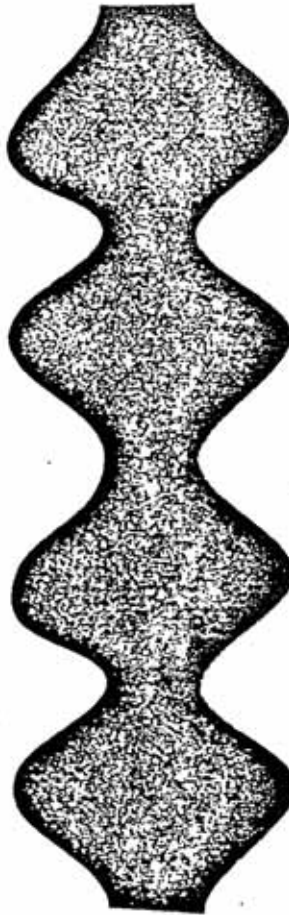
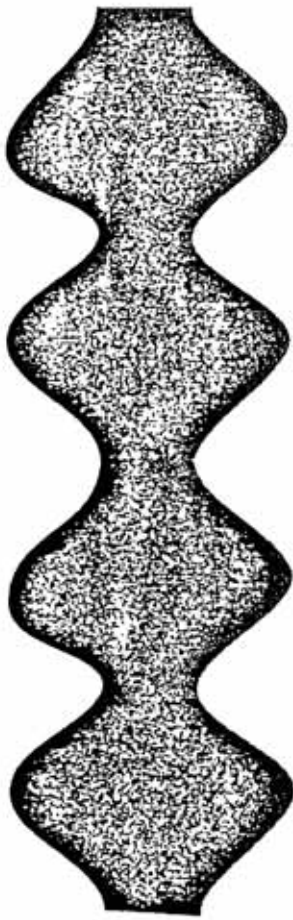
30 sec  
30 sec den 60 sec  
period - .87um

Gave to Alfons for  
reaction in 0

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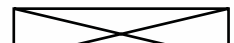




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3 Sept 92

Fig 9



OPTION 1

Commercialization of this subject invention should not negatively impact national security but should strengthen the ability of the country's economic leadership.

OPTION 2

Commercialization of this subject invention should not negatively impact national security but should support the national economic vitality.

OPTION 3

Commercialization of this subject invention should not negatively impact national security but should help the US to meet the international economic challenge.

OPTION 4

Commercialization of this subject invention should not negatively impact national security but should assist the US industry become more successful in meeting the global economic challenge.

OPTION 5

strengthen Nation's leadership position in economic growth, scientific advance, and technological innovation

OPTION 6:

The subject invention has government and industry applications, especially in \_\_\_\_\_ . Such applications do not compromise national security but should strengthen the country's economic competitiveness and permit Sandia to cooperate with DOE in effective technology transfer.

The subject invention has government and industry applications, especially in \_\_\_\_\_ . Such applications do not comp