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Graphoepitaxy

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FOR THE COMMANDER

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GRAPHOEPITAXY.

⑨ SEMIANNUAL TECHNICAL SUMMARY REPORT, 1 Jul - 31 Dec 79,

TO THE

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ABSTRACT

A new technique for fabricating high-contrast x-ray masks with simple patterns of lines and spaces less than 50 Å in width is described. The successful replication of 175-Å lines and spaces in polymethyl methacrylate (PMMA) using the carbon K (45-Å) x-ray is reported. It was found that PMMA structures smaller than 150 Å in width lost their physical integrity and would not adhere to SiO_2 substrates.

CONTENTS

INTRODUCTION

The objectives of this research program for calendar year 1979, as stated in the proposal for renewal dated 16 October 1978, were:

(a) Determine if surface-relief structures in SiO_2 or Si_3N_4 can induce oriented single-crystal growth of silicon and/or gallium arsenide.

(b) Conduct basic studies, by transmission microscopy (TEM), of thin-film nucleation and growth on surface-relief structures.

(c) Conduct studies of laser annealing of silicon and gallium arsenide over surface-relief structures in SiO_2 and Si_3N_4.

(d) Improve technology of surface-relief-structure fabrication to provide finer spatial periods, sharper corners, smoother sidewalls, and straighter edges.

Objective (a) was achieved in the fourth quarter of 1978: uniformly oriented crystalline films of silicon were produced by laser crystallization of amorphous silicon over surface-relief gratings in amorphous SiO_2. As a result of this success, the objectives for calendar year 1979 were as follows:

(a) Improve the crystallographic and electrical properties and the surface smoothness of silicon produced by graphoepitaxy.*

(b) Conduct basic studies, by TEM, of thin-film nucleation and growth on surface-relief structures [same as (b) above].

(c) Develop means of achieving graphoepitaxy of Si and GaAs that do not involve laser crystallization.

(d) Improve technology of surface-relief-structure fabrication to provide finer spatial periods, sharper corners, smoother sidewalls, and straighter edges [same as (d) above].

(e) Fabricate simple diodes and transistors in Si and/or GaAs oriented by graphoepitaxy.

This report describes progress on item (d).

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* A new term we coined for the process of orienting overlayer films by means of surface-relief patterns.

GRAPHOEPITAXY

REPLICATION OF 175-Å LINES AND SPACES IN POLYMETHYL METHACRYLATE USING X-RAY LITHOGRAPHY

The ultimate resolution of x-ray lithography is limited by diffraction, the intrinsic resolution of the x-ray sensitive resist, and the range of photoelectrons excited in the resist when an x-ray photon is absorbed.[1] To minimize diffraction one would want to minimize x-ray wavelength; however, photoelectron range increases as x-ray wavelength decreases. The carbon K (45-Å) x-ray represents a near optimum compromise between these conflicting requirements. The effective range of photoelectrons excited in polymethyl methacrylate (PMMA), the x-ray resist with the highest known resolution, by the carbon K x-ray is believed to be less than 50 Å, and in thin PMMA the limit of resolution due to diffraction should be comparable.[2] In addition, there are significant practical reasons for using the carbon K x-ray: polymer materials, such as polyimide, with attenuations of 2 dB/µm are available from which low-absorption mask membranes can be made, and x-ray absorbers with attenuations as high as 170 dB/µm exist.[3] In this report, a new technique for fabricating high-contrast x-ray masks with lines and spaces smaller than 50 Å is described, and the replications of 175-Å-wide lines and spaces in PMMA on thick SiO_2 substrates is reported.

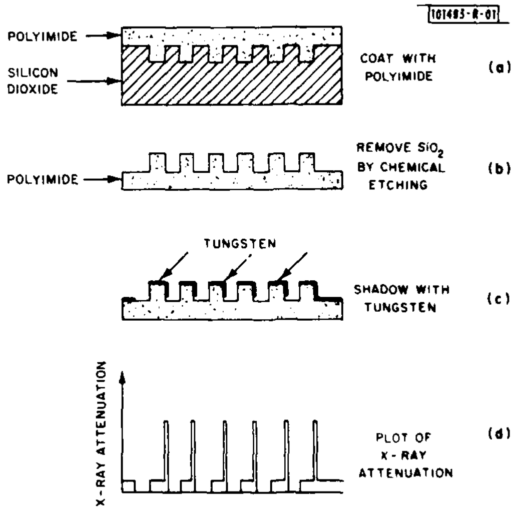

Fig. 1. Sequence of steps for fabricating a narrow-linewidth high-contrast x-ray mask by shadowing a polyimide surface-relief structure. The silicon dioxide "mold" in step (a) is made by reactive-ion etching using CHF_3 gas. The lower portion of the figure shows the attenuation of x-rays passing through the completed mask at normal incidence.

A simple procedure for fabricating an x-ray mask having very narrow and well-controlled lines is illustrated in Fig. 1. A square-wave grating with smooth vertical sidewalls is fabricated in SiO_2 using x-ray lithography, chromium liftoff, and reactive-ion etching as described in an earlier paper.[4] The square-wave structure is transferred into polyimide plastic by spin coating the SiO_2 relief structure with a liquid solution of a polyimide precursor[5] followed by baking to polymerize the coating. The polyimide membrane is then either peeled from the SiO_2 structure after release in diluted HF, or the SiO_2 substrate is etched away in concentrated HF. The

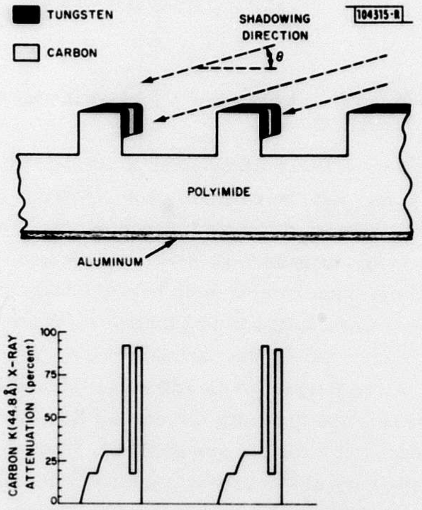

Fig. 2. The cross section of an x-ray mask with narrow lines and spaces is shown. High-attenuation lines separated by low-attenuation spaces are made by alternately shadowing the polyimide structure with tungsten (158-dB/μm absorption) and carbon (2-dB/μm absorption). The aluminum film on the back of the polyimide membrane serves as an electrical contact for the electrostatic hold-down scheme used to maintain intimate contact between the mask pattern and a PMMA resist film during x-ray replication. The lower part of the figure shows the attenuation of carbon x-rays passing through the x-ray mask at normal incidence. The uniform attenuation of the polyimide membrane and the aluminum film is ignored in this plot.

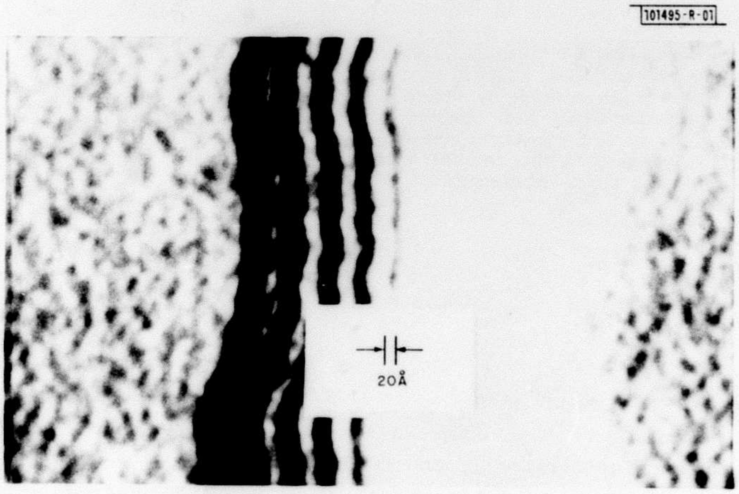

Fig. 3. TEM of an x-ray mask fabricated by the shadowing technique shown in Fig. 2 demonstrating the extremely narrow linewidths that can be obtained. Five nearly opaque tungsten lines are separated by four essentially transparent carbon spaces. The tungsten lines are approximately 300 Å thick and the narrowest line is about 20 Å wide.

completed polyimide membrane with its square-wave relief structure is mounted onto a metal ring holder using epoxy. The polyimide relief structure is then shadowed at an oblique angle with x-ray absorber material.

The attenuation for carbon K x-rays passing through the mask at normal incidence is shown in Fig. 1(d). The linewidth of the high-contrast region of the mask can be determined very precisely (±<5 Å) since the thickness of the absorber material can be accurately controlled using conventional thin-film techniques.[6] By shadowing the polyimide relief structure alternately with x-ray absorber and x-ray transparent material (as shown in Fig. 2), a high-contrast mask can be made having lines and spaces less than 50 Å in width. Figure 3 shows a transmission electron micrograph (TEM) of an x-ray mask made by this procedure having tungsten lines and carbon spaces as narrow as 20 Å. Tungsten was chosen as the absorber material in these experiments because it has a small grain size and high x-ray attenuation (158 dB/μm).[3] Carbon was chosen for the transparent spaces because it is amorphous and has an attenuation of only 2 dB/μm.

X-ray masks made by the square-wave shadowing technique were used to investigate the resolution limits of x-ray lithography at the carbon K wavelength. The SiO_2 relief structures used were gratings of 3200-Å spatial period, ~1600-Å linewidth, with depths of 1000 Å. The polyimide coatings were ~1 μm thick. A mask having 200-Å-wide tungsten lines was produced by a single shadowing of the polyimide using the procedure of Fig. 1. Also, a multiply shadowed mask with ~175-Å-wide tungsten lines and carbon spaces was produced using the procedure depicted in Fig. 2. These masks were replicated in PMMA using carbon K x-rays. PMMA of 950,000 average molecular weight was used in all the experiments.[7] The developer consisted of a mixture of 40% methyl isobutyl ketone and 60% isopropyl alcohol. The mask and PMMA coated substrate (a silicon wafer coated with 5000 Å of thermally grown SiO_2) were held in intimate contact by applying 30 V between the silicon wafer and a 400-Å-thick aluminum film on the smooth side of the x-ray mask. Carbon K x-rays were generated by a conventional electron bombardment type source* operated at 4.7 kV and 70 mA. The source diameter was about 1 mm and the source-to-substrate distance was 6 cm. An exposure time of 240 min. resulted in PMMA development rate of ~30 Å/s in areas corresponding to the low attenuation regions of the tungsten absorber pattern [see Fig. 1(d)]. The PMMA was developed until only the pattern of fine lines, corresponding to the high attenuation regions, remained. Preshadowed carbon replicas[8] of the PMMA structures were examined in a TEM. This examination technique was necessary because the resolution of a conventional scanning electron microscope (SEM) is inadequate. Figure 4 shows a TEM micrograph of a preshadowed carbon replica of a 200-Å-wide, 600-Å-high PMMA line on an SiO_2 substrate exposed using the single-shadowed mask. Figure 5 shows a TEM micrograph of a preshadowed carbon replica of two 175-Å-wide PMMA lines separated by 175 Å on an SiO_2 substrate. These were exposed using the multiple-shadowed mask. Perspective views depicting the original PMMA structures, as determined from TEM micrographs of the preshadowed carbon replicas, are also shown in Figs. 4 and 5. To demonstrate that these PMMA structures should be useful for device fabrication or applications requiring a mask material more durable than PMMA, a pattern in thin tungsten was produced by the liftoff process using PMMA structures similar to those shown in Fig. 5. A TEM micrograph of the tungsten pattern obtained is shown in Fig. 6.

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* EG-1, Vacuum Generators Limited, Sussex, England.

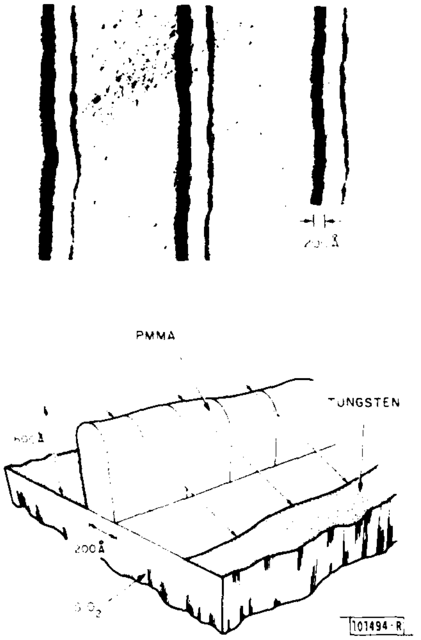
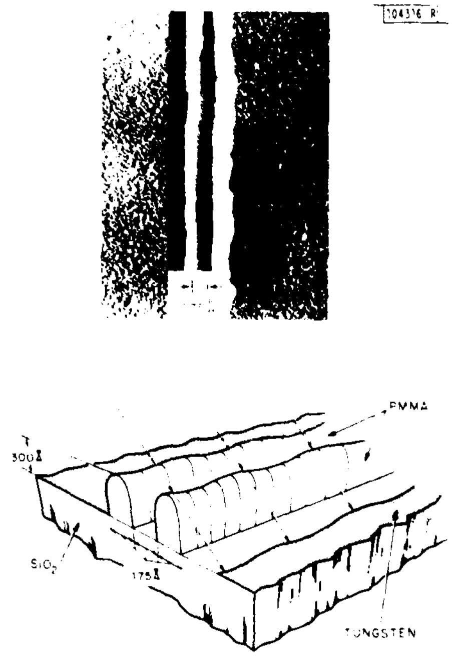


Fig. 4. TEM of a preshadowed carbon replica of a 200-Å-linewidth, 600-Å-high PMMA pattern on an SiO_2 substrate, produced by replicating a mask fabricated by the procedure of Fig. 1 using the carbon K (45-Å) x-ray. The PMMA structure was shadowed at 45° with 25 Å of tungsten before the carbon replica of the structure was made to increase contrast in the electron microscope. The lower half of the figure is a perspective view of the PMMA structure as determined from the TEM.

Fig. 5. TEM of a preshadowed carbon replica of two 175-Å-wide, 300-Å-high PMMA lines separated by a 175-Å-wide space on an SiO_2 substrate, produced by replicating a mask fabricated by the procedure shown in Fig. 2 using the carbon K x-ray. To increase contrast in the electron microscope the PMMA structure was shadowed at 45° with 25 Å of tungsten before the carbon replica was made. A perspective view of the PMMA structure as determined from the micrograph is shown in the lower half of the figure.



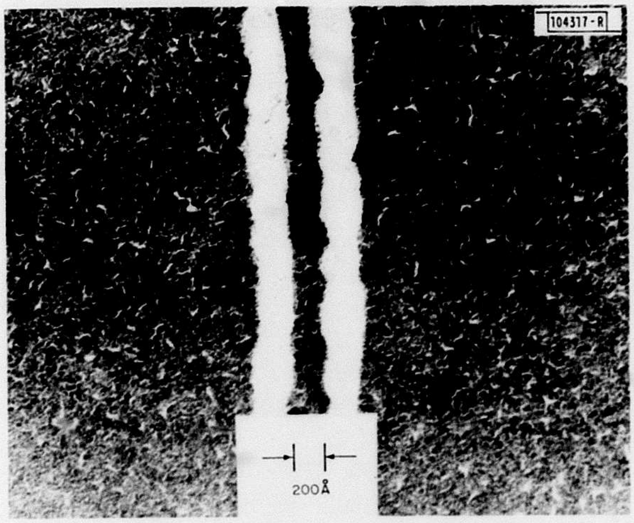


Fig. 6. TEM of a 50-Å-thick electrically continuous tungsten pattern on an SiO_2 substrate produced by liftoff using a PMMA pattern similar to that shown in Fig. 5. Tungsten was evaporated onto the structure at normal incidence and the PMMA was dissolved in monochlorobenzene.

Scaling of diffraction calculations and results of contact lithography at optical wavelengths[9] to the x-ray regime indicates that it should be possible to replicate lines and spaces narrower than 75 Å in 200-Å-thick PMMA using the carbon K x-ray. The minimum linewidth obtained in the present work was 150 Å. At linewidths narrower than this, the PMMA lines appear to lose adhesion to the substrate or simply disintegrate. Similar problems have been observed in electron beam exposure of PMMA films on thin gold-coated Si_2N_4 foils: lines smaller than 200 Å appear to lose adhesion.[10] The reason for this loss of adhesion is unclear; possibly the mechanism of PMMA adhesion fails at these linewidths.[11]

The technique for fabricating x-ray masks by shadowing a relief structure in polyimide with an x-ray absorber can be extended to structures other than square wave. The use of triangular cross-section structures is described in another publication.[12] In that case, anisotropic etching of single-crystal silicon provides the mold. A major advantage of the technique using triangular cross-section structures is precise control of line-to-space ratio in periodic gratings. Linewidths as fine as 400 Å and periods of 1968 Å have been reported with linewidth control of about ±50 Å.

Absorber patterns of arbitrary geometries (e.g., contact pads), produced by more conventional methods, can be superimposed over or combined with the simple patterns of fine lines (i.e., lines, gaps, interdigitated structures, etc.) produced by shadowing techniques to yield structures that could be used as devices. Applications include Josephson microbridges,[13] planar superlattices,[14] investigations of transport in narrow conductors,[15] graphoepitaxy,[16] electrode structures for subcellular probing, and structures for large molecular manipulation (e.g., for purpose of observation[17] or for supermolecular structure synthesis).

D. C. Flanders

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