



157 nm Resist Development Project (LITJ103) Year-End Report

SEMATECH and the **SEMATECH logo** are registered service marks of SEMATECH, Inc.
International SEMATECH and the **International SEMATECH logo** are registered service marks
of International SEMATECH, Inc., a wholly-owned subsidiary of SEMATECH, Inc.

Product names and company names used in this publication are for identification purposes only
and may be trademarks or service marks of their respective companies.

157 nm Resist Development Project (LITJ103) Year-End Report

Technology Transfer # 00114031A-ENG

International SEMATECH

November 30, 2000

Abstract: This report summarizes year 2000 activities of the LITJ103 project, 157 nm Resist Development. The 157 nm Exitech exposure tool, resolution enhancement, and outgassing projects are discussed. A list of presentations and the procedure for submitting samples to the Resist Test Center (RTC) are included in the appendices.

Keywords: Materials Testing, Lithography Equipment, Phase Shifting Masks, Resists, Outgassing, Photoresists

Authors: Kim Dean

Approvals: Gene Feit, Program Manager
Kim Dean, Project Manager
Gerhard Gross, Director
Laurie Modrey, Technical Information Transfer Team Leader

Table of Contents

1	EXECUTIVE SUMMARY.....	1
2	INTRODUCTION.....	1
3	157 NM EXITECH EXPOSURE TOOL.....	1
	3.1 157 nm Resolution Enhancement	4
	3.2 157 nm Resist Outgassing.....	5
	APPENDIX A: LIST OF PRESENTATIONS.....	7
	APPENDIX B: PROCEDURES TO SUBMIT RESIST SAMPLES FOR 157NM TESTING AT INTERNATIONAL SEMATECH.....	8

List of Figures

Figure 1	Current Performance of Exitech	3
Figure 2	Dipole Results	4
Figure 3	Phase Shift Mask Results.....	5

Acknowledgements

The following were team members on this project:

Wolf-Dieter Domke

Steve Bassett

Hyeong Soo Kim

Stefan Hien

D.C. Owe Yang

1 EXECUTIVE SUMMARY

Project LITJ103, 157 nm Resist Development, provides engineering support for 157 nm resist development in the Resist Test Center (RTC). In 2000, the major tasks included installing the 157 nm Exitech exposure tool, resolution enhancement of the Exitech tool, and resist outgassing studies at Massachusetts Institute of Technology's Lincoln Laboratories (MIT LL) and International SEMATECH. The tool was accepted and made available to RTC customers in June 2000. The resolution enhancement techniques have extended the resolution of the tool down to 90 nm 1:1 features. To protect the lens, a protocol has been established for testing resists for outgassing.

2 INTRODUCTION

Currently, no commercial 157 nm photoresist system is available to member companies for evaluating exposure tools or producing 70 nm prototype devices. The member companies are most interested in single layer resists (i.e., resists that provide the primary etch resistance for substrate etches). The objective of this project is to provide member companies with prototype 157 nm single layer resists by end of 2001 for tool testing and pilot line device fabrication.

The project has two phases. In phase one, from the inception of the project (September 1999) through mid-2001, the project provides engineering support for 157 nm processing at the RTC. This includes the procurement, installation, acceptance, and process/equipment support of the 157 nm Exitech exposure tool in the RTC; early resist supplier development; and resist outgassing studies. The second phase includes 157 nm resist benchmarking, supplier commercialization support, and the beginning of procurement of an extreme ultraviolet (EUV) micro exposure tool (MET).

The project has been described at the resist advisory group (RAG) meetings in January, May, and September 2000. The presentations are listed in Appendix A.

3 157 NM EXITECH EXPOSURE TOOL

In spring 1999, a request for quotes and specifications was sent to all exposure tool manufacturers. The quotes were evaluated based on schedule, performance, and cost. Exitech Limited of Oxford, England, was awarded the purchase, and the tool was delivered to International SEMATECH in December 1999.

During the installation, some issues delayed the schedule:

- Autofocus stability problems
- Contamination of the illuminators and lens

The autofocus stability problem was solved by changing the design of the nose cone on the lens. After experimenting with several different nose cones, the proper balance of purge gas flow was achieved to keep the autofocus stable and get the desired low O₂ content.

The contamination problems proved to be more difficult to solve. The illuminator contamination problems included the following:

- Visible deposition on refractive elements and partial coherence aperture in the relay group
- Deposit confined to the 157 nm irradiated areas

- Transmission drop of refractive elements from ~90% to ~60%
- Transmission of the illuminator reduced to 12% of the initial transmission over 5 million pulses
- Deposited film of ~150 Å thickness as measured with an ellipsometer
- Deposited material removable using solvent or ozone cleans
- X-ray photoelectron spectroscopy (XPS) analysis determined the major contaminant was organic, quantified as 6.4% F, 15.9% O₂, 2.5% N₂, 0.5% Ca, 72.4% C, and 2.2% S
- Secondary ion mass spectroscopy (SIMS) analysis determined the major organic contaminants as nitrogen containing compounds including amine and amide. Trace levels of calcium, fluorine, sodium, potassium & chlorine were detected.

The cause of the contamination was never completely understood. As a precautionary measure, point-of-use filters were installed for the nitrogen purge lines. New illuminators were provided, and the transmission has been stable for over 60 million pulses.

Only 200 nm 1:1 images were initially obtained; 180 nm 1:1 images were achieved after alignment optimization work (well short of the 130 nm 1:1 specification). Also, the transmission through the lens was reduced to 80% of the initial transmission value over 5 million pulses. When the lens was removed, contamination was found on the objective lens. It could not be removed by solvents; it could be removed only by polishing. The cause of the contamination was suspected to be resist outgassing, but no direct evidence supported this supposition. A new lens was provided; the transmission and imaging has been stable over 35 million pulses.

The acceptance test was completed on June 17, 2000. The tool passed all tests except across field uniformity. This test was repeated at a later date with an improved resist process and the specifications being met. More details on the acceptance are available from the Exitech review at the September RAG (see Appendix A).

The tool was released to the RTC on June 20, 2000. Its current performance exceeds the resolution specification of the tool (130 nm 1:1). See Figure 1.

- System was accepted on June 20th 2000.
- These images were taken during the first visit by a commercial resist supplier (June 28th 2000).
- Resist 70 nm thick, Shipley XP-23332-C.

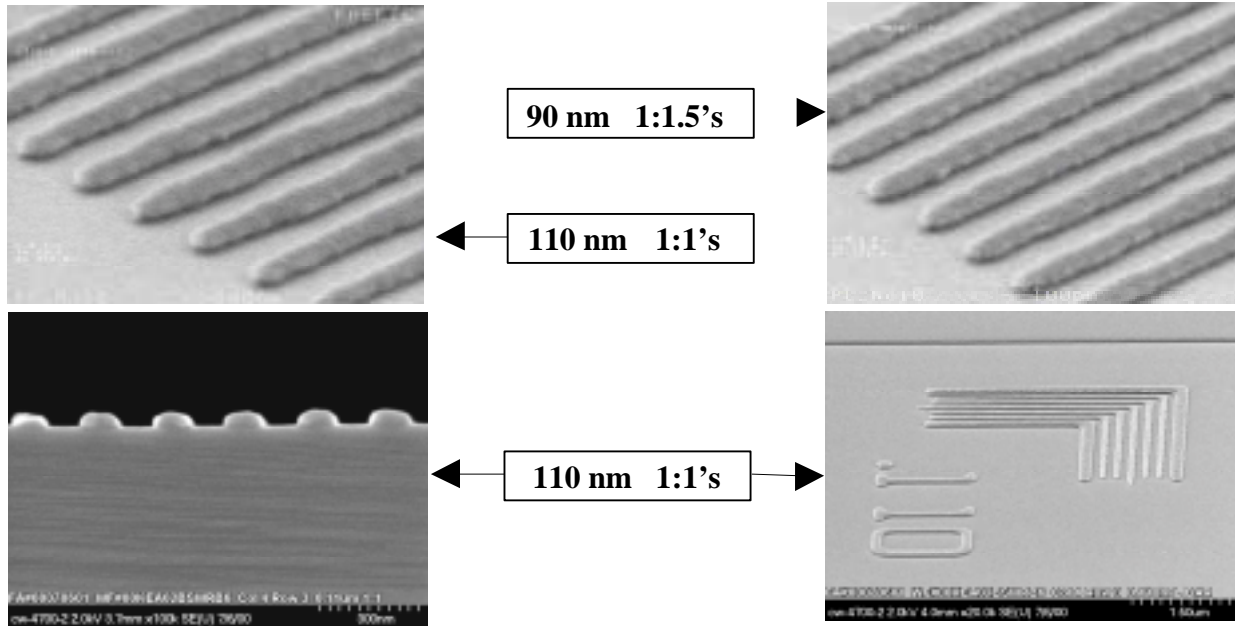
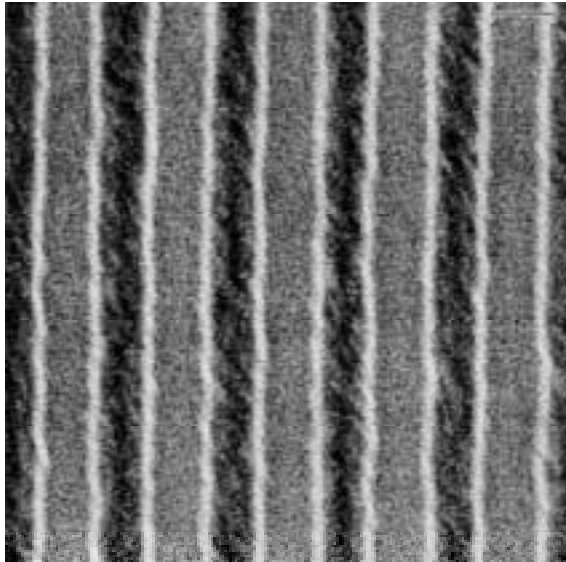


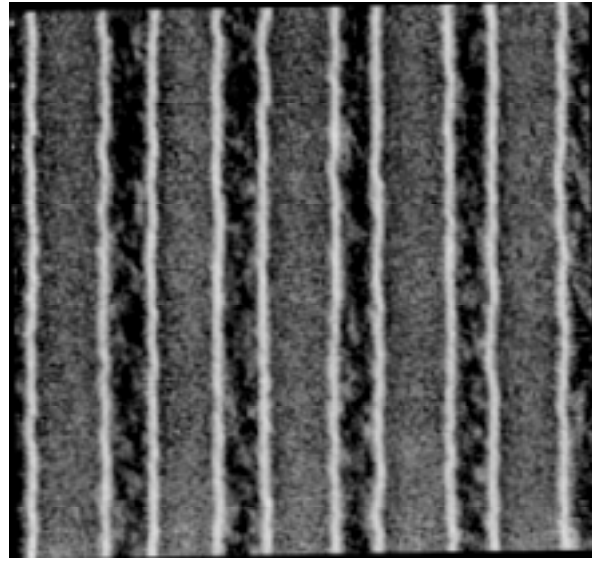
Figure 1 Current Performance of Exitech

3.1 157 nm Resolution Enhancement

Several apertures for the Exitech tool were made and a phase shift mask designed. The mask blanks were made by Ashai, the coatings were deposited by Hoya, and the mask was patterned by Infineon. The resolution was improved with the dipole aperture; 90 nm 1:1 features were imaged (see Figure 2). Similar performance was obtained with the phase shift mask (see Figure 3).



90 nm 1:1's
 $K_1 = 0.34$



70 nm 1:1.5's
 $K_1 = 0.33$

Conditions:

- **Illumination Aperture:** Dipole $0.2\sigma / 0.7\sigma$.
- **Exposure Tool:** Exitech 157 nm Microstepper, 0.6NA Tropel Lens (1.5x 1.5 mm field size).
- **Mask:** Binary (Chrome on modified fused silica - Asahi).
- **Resist:** Shipley 32C, 70 nm Thick, 5 mJcm^{-2} dose.
- **Substrate:** Silicon.

Figure 2 Dipole Results

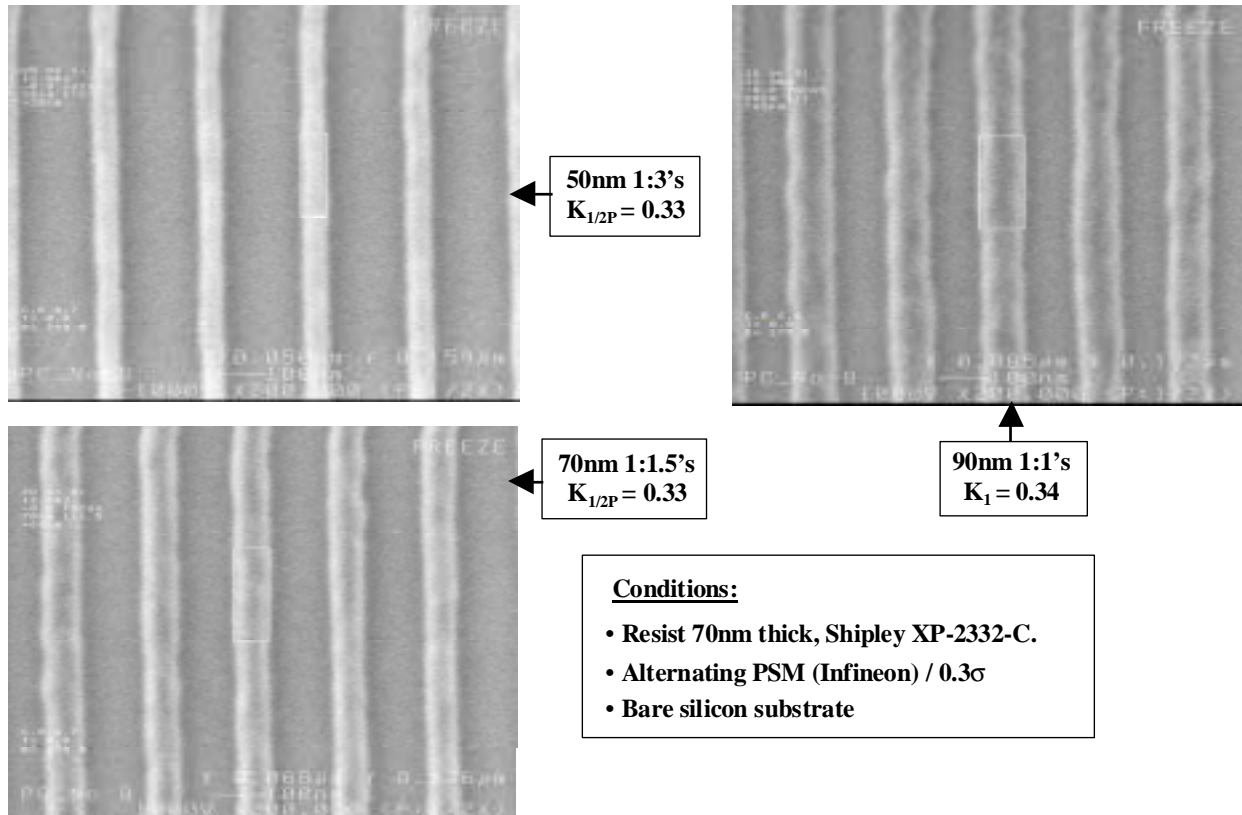


Figure 3 Phase Shift Mask Results

3.2 157 nm Resist Outgassing

This project is an extension of LITH103, 193 nm Resist Outgassing, with MIT LL.

Seventeen resists have been tested at MIT LL. To date, these are the major conclusions:

- The absolute amount of organic contamination outgassed during 157 nm exposure of existing resists does not differ greatly from 193 nm resists.
- The mechanism at 157 nm favors direct photolysis, resulting in a greater probability for higher pressure transients.
- Fluorine resists look acceptable; the outgassing rates are virtually indistinguishable from their organic analogs. The rates and compounds indicate that environment, safety, and health (ESH) concerns should be minimal.
- Some silicon resists raise concerns. Silyl-functionalized acrylics exhibit side-chain cleavage. There does not appear to be a problem with main-chain silicon.
- Photochemistry of these polymers dominates the outgassing behavior; thermal decomposition is negligible until fluences $> 1 \text{ mJ/cm}^2$.

International SEMATECH is also conducting 157 nm resist outgassing studies to protect the 157 nm Exitech microstepper from resist outgassing deposition. As a result of this work, a procedure is now in place to screen resists before they are exposed on the imaging stage of the Exitech. (The procedure is in Appendix B.) There are three methods for testing resist for outgassing:

1. Film thickness loss after exposure—the resist passes if the loss is below 5 nm.
2. Chemical analysis of outgassing components (conducted by MIT LL, as described above)—the resist passes if Si compounds are detected below $2 * 10^{10}$ molecules/cm²/s.
3. CaF₂ proof-plate test (proof of resist outgassing deposition using the open frame stage of the 157 nm Exitech)—the resist passes if the transmission change < 1.0 % and if Si-content (XPS) < 0.5 %.

Lens-cleaning experiments have also been investigated at SEMATECH and at MIT LL. Depositions have been made with plasma sources and with the CaF₂ proof-plate. The conclusions are as follows:

- Typical cleaning rates at 50 ppm O₂ are 1.0 nm/10 J/cm² (MIT LL data)
- Cleaning experiment at SEMATECH at 10 ppm O₂ yielded 0.2 nm/J/cm²
- F-containing deposits can be cleaned off under 157 nm irradiation
- Si-containing materials can NOT be cleaned with 157 nm irradiation

The nitrogen purge near the lens is also being investigated in an effort to protect the lens. Sandia National Laboratories will model the purge air flow of the lens nose cone. Based on the models, new nose cones for the Exitech will be designed and tested.

The overall conclusions of the outgassing work are as follows:

- Resist outgassing is a serious issue at 157 nm.
- Critical materials have been identified.
- Pass/fail criteria for Resist Test Center have been developed and are being used in a manner to run as many materials as possible.
- Risk management allows the use of critical materials at low imaging doses.
- Resist deposits have been identified and cleaning procedures were tested.
- Results indicate the need for deep and profound understanding of the mass transport of outgassing material near the lens. Optimizing the lens purge in terms of resist outgassing is important.

APPENDIX A: LIST OF PRESENTATIONS

LITJ103 Overview, Jan. 2000 RAG
Exitech Review, Jan. 2000 RAG
MIT LL Outgassing, Jan. 2000 RAG
Resist Processing at 157 nm, 157 nm Symposium, Dana Point, CA, May 2000
LITJ103 Overview, May 2000 RAG
Exitech Review, May 2000 RAG
MIT LL Outgassing, May 2000 RAG
LITJ103 Overview, Sept. 2000 RAG
Exitech Review, Sept. 2000 RAG
ISMT Outgassing, Sept. 2000 RAG
MIT LL Outgassing, Sept. 2000 RAG
Resolution Enhancement, Sept. 2000 RAG
Exitech Review, 157 nm Technical Data Review, San Diego, CA, Nov. 2000

APPENDIX B: PROCEDURES TO SUBMIT RESIST SAMPLES FOR 157NM TESTING AT INTERNATIONAL SEMATECH

1. Contact your host and tell them that you would like time on the 157 nm microstepper. If you do not have a host, contact Kim Dean at (512) 356-3275. If the formulations have already been tested for outgassing at 157 nm here at International SEMATECH, schedule time on the Resist Test calendar.
2. Send Material Safety Data Sheets (MSDS) for each formulation by email to your host as soon as possible. It will take the ESH department 4 days to approve the MSDS and give the host chemical authorization numbers. (These numbers are used to keep track of approved chemicals on site.) The host will complete a no charge purchase requisition and then a purchasing agent from SEMATECH will contact the supplier so that the resist(s) can be shipped. This requires another day. Therefore, we need at least 5 business days from the time we receive the MSDS until you can ship the chemicals.
3. If the formulations have not been evaluated at International SEMATECH before, the host will arrange a teleconference with Kim Dean and/or Stefan Hien to discuss the outgassing/deposition tests. This should occur within 2–5 days.
 - a. In the teleconference, we will discuss the three outgassing/deposition tests. We will discuss some details of the formulation; if we have tested similar formulations, then we may not have to do outgassing tests. We may ask about polymer type (acrylic, “ESCAP,” siloxane, etc.), blocking groups and photoacid generators. Only Stefan Hien and Kim Dean will use this information in order to determine if the material needs to be tested. If we decide to test the materials for outgassing/deposition, please have the host arrange time on the Resist Test Center (RTC) calendar (approximately 3–4 samples can be evaluated in one shift). You do not have to be here for these tests.
 - b. The first outgassing test will measure the resist loss after exposure with an array from 1 to 100mJ/cm². The maximum tolerated film thickness loss for exposures on the imaging side are 5 nm. With this test, we obtain the maximum dose for each material (for example, with poly-t-butylmethacrylate, we measure 30 nm film thickness loss at 100 mJ/cm²; therefore, at 16.7 mJ/cm² we have a film loss of 5 nm). In general, we prefer a photospeed of 10 mJ/cm² or less and a film thickness loss less than 1 nm at the dose to print.
 - c. The second test is the 157 nm outgassing procedure at MIT/LL under SEMATECH’s project. Not all formulations will be sent to MIT/LL; only new and novel materials will be sent. If we decide to use this test, the supplier will send the samples directly to MIT, along with the MSDS. International SEMATECH will share some of the data with the member companies; an example is shown on the next page. You will receive a full report for the resist that you submit for testing. With this test, the overall outgassing rate can be determined and the fragmentation during irradiation can be studied. Critical molecular species like Si-compounds or aromatic fragments can be identified. Furthermore, these investigations help interpret the CaF₂ deposition test (3d). The tests at MIT/LL and at SEMATECH will happen in parallel.

- d. The third outgassing test uses a CaF₂ plate on the open frame exposure stage of the 157 nm microstepper. We expose 4 wafers for the test at a constant dose of 50 mJ/cm². The CaF₂ plate is removed and the transparency is compared to the original transparency for that plate. If the transmission decreases by >1%, then the outgassing is too high. Also, if silicon is detected (by XPS of the plate), the resist fails. Nevertheless, limited experiments can be carried out if the resist is used below exposure doses where the test would yield XPS-Si signals below 0.5%. A typical value for polysiloxanes (Si in main chain) is 0.5% at 50 mJ/cm². A typical value for silicon in the side chain is 6% Si signal for 10% silicon containing material (this was observed with different compounds).
- e. If the formulations fail the test from step 3b or 3d, we will not allow the resist to be imaged on the tool. If this happens, we will work with the supplier to try and improve the formulations for reduced outgassing.
- f. The supplier has to inform International SEMATECH about any known amount of silicon, even in very small quantities (ppb).
- g. If the formulations pass, have your host schedule time on the RTC calendar for your visit.

**International SEMATECH Technology Transfer
2706 Montopolis Drive
Austin, TX 78741**

**<http://www.sematech.org>
e-mail: info@sematech.org**