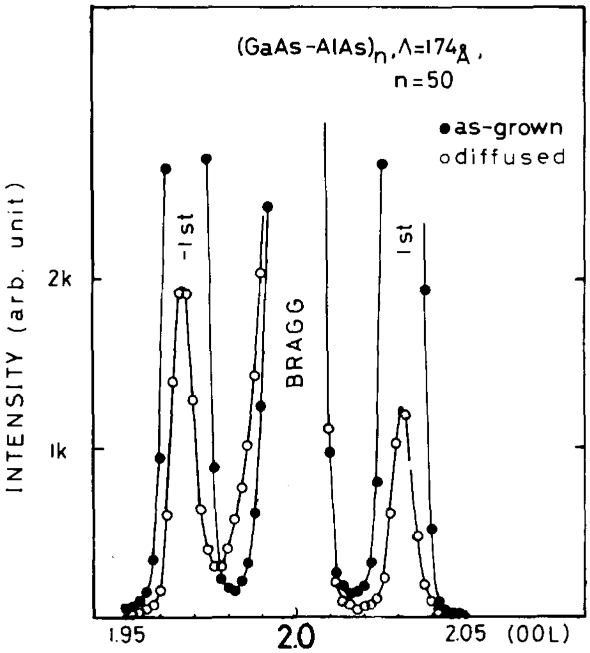

FIG. 3. Asymmetric diffraction profile of the (002) reflection observed in the sample after Zn diffusion at 590 °C. The local lattice expansion around a Zn atom can be seen at the tail of the (002) reflection.

out the multilayer in the early stage of annealing where the Zn-diffused stripes[3] are observed optically.

The x-ray diffraction profiles after Zn diffusion were carefully examined. The tail of the (002) reflection becomes asymmetric after the diffusion as shown in Fig. 3, implying the local lattice expansion around a Zn atom or a Zn-vacancy pair.[3] To clarify the local structure around a Zn atom, we attempted the measurement of an extended x-ray absorption fine structure (EXAFS) near the Zn-K edge with synchrotron radiation of a 2.5-eV storage ring in the National Laboratory for High Energy Physics (KEK, Tsukuba). However, we could not determine the local structure around a Zn atom because of the low concentration of Zn in the sample.

The enhancement of the Ga-Al interdiffusion by Zn may be due to a modification of the interstitial-substitutional mechanism.[8] Ladig *et al.*[3] proposed a Zn-vacancy pair formed by substitutional Zn. The impurity-vacancy pair will eventually give the diffuse x-ray scattering.[9,10] Recently the kinetics of the growth law for the domain size L near the several phase transitions have been discussed.[11] A power-law form, $L \propto t^{y}$, is proposed ($y = 1/2$ for density not conserved) and the diffraction profile can be cast in scaled form. The careful measurements of the diffuse x-ray scattering in the annealed samples of a GaAs-AlAs superlattice are in progress.

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[1] L. L. Chang and A.Koma, Appl. Phys. Lett. **29**, 138 (1976).
[2] R. M. Fleming, D.B. MoWhan, A. C. Gossard, W. Wiegmann, and R. A. Logan, J. Appl. Phys. **51**, 357 (1980).
[3] W. D. Laidig, N. Holonyak, Jr., M. D. Camras, K. Hess, J. J. Coleman, P. D. Dapkus,and J. Bardeen, Appl. Phys. Lett. **38**, 776 (1981).
[4] S. W. Kirchoefer, N. Holonyak, Jr., J. J. Coleman, and P. D. Dapkus, J. Appl. Phys. **53**, 766 (1982).
[5] L. L. Chang, Solid State Electron. **5**, 853 (1964).
[6] Y. Yamamoto and H. Kanbe, Jpn. J. Appl. Phys. **19**, 121 (1980).
[7] Y. Matsumoto, Jpn. J. Appl. Phys. **22**, 829 (1983).
[8] H. C. Casey, in *Atomic Diffusion in Semiconductors*, edited by D. Shaw (Plenum, New York, 1973), p. 351.
[9] H. Terauchi and J. B. Cohen, J. Phys. Chem. Solids **39**, 681 (1978).
[10] T. Terauchi and J. B. Cohen, Phys. Rev. B **17**, 2494 (1978).
[11] A. Sadiq and K. Binder, Phys. Rev. Lett. **51**, 674 (1983).

Polymethyl methacrylate resist sensitivity enhancement in x-ray lithography by *in situ* polymerization

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X-ray-induced grafting of acrylic acid to poly (methyl methacrylate) (PMMA) increases the resist sensitivity by at least three orders of magnitude. Scanning electron microscopy of grafted PMMA revealed micron and submicron features for dose levels as small as 0.1–1 mJ/cm^2, thus demonstrating the possibility of using this technique for x-ray lithography.

PACS numbers: 81.60.Jw, 82.50. – m, 61.80.Cb, 82.35. + t

A limitation of x-ray lithography is the inability to create patterns at high speeds. The sensitivity of the resist to incident radiation is one component of this limitation. For this reason, many researchers have concentrated on developing more sensitive resists by changing the chemical structure of the resist.[1,2]

Poly (methyl methacrylate) (PMMA) is a well known electron beam and x-ray resist with excellent resolution, fair-

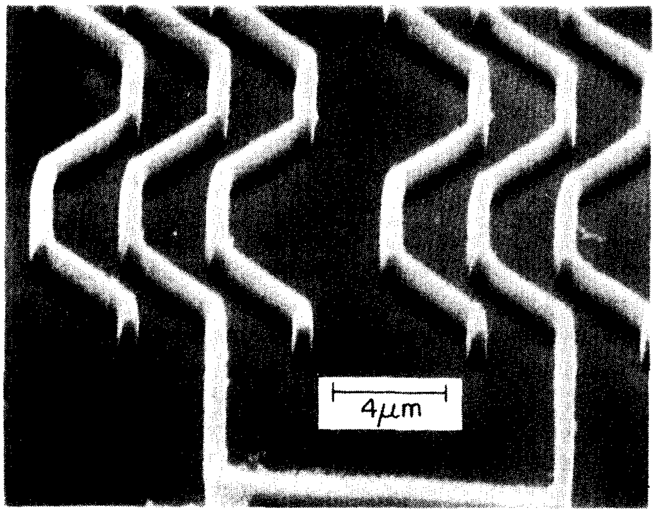

FIG. 1. Electron micrograph of PMMA exposed at an x-ray dose of 1 J/cm^2.

ly good plasma etch resistance, and good process compatibility, but suffers from low sensitivity to either form of radiation. Generally, doses from 0.5–2 J/cm^2 are required for different x-ray sources.[3] This letter reports results obtained by the technique of *in situ* polymerization which enhances resist sensitivity by three orders of magnitude,to the level of ~ 1 mJ/cm^2. We have recently reported[4] that a similar sensitivity enhancement can be attained with 25 keV electron beam irradiation.

The x rays interact with PMMA and produce Auger electrons and photoelectrons, which in turn break the chemical bonds of PMMA molecules forming free radicals. These intermediate radicals lose their energy through processes in which smaller molecules are obtained.[5] This behavior is the basis of the positive resist process. However, if new monomer is introduced into the system before the free radicals lose their activity, a new chain reaction may be initiated.[6] As a result of this occurrence, a copolymer (block or graft) of PMMA and the monomer is obtained. This copolymer is unlike the starting material because it is structurally modified by copolymerization and exhibits different chemical properties than PMMA. If the solubility of the copolymer strongly differs from that of PMMA, patterns can then be delineated by subsequent solvent development. If copolymer formation is more sensitive to irradiation than the normal degradative process, image amplification can occur.

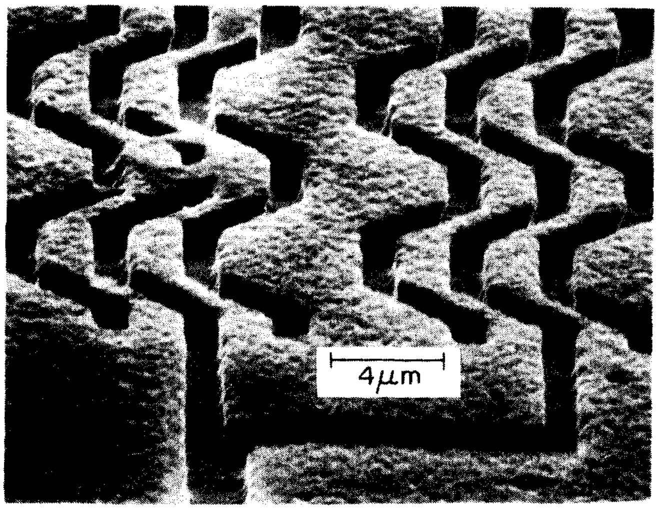

FIG. 2. Electron micrograph of PMMA grafted with acrylic acid after exposure to an x-ray dose of 1×10^{-3} J/cm^2.

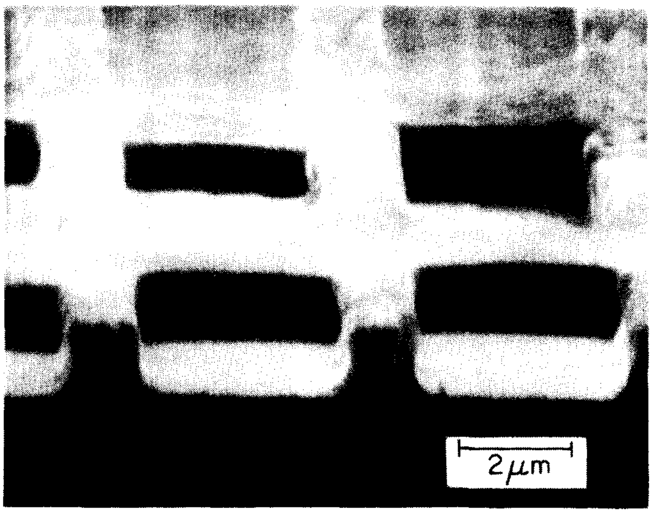

FIG. 3. High magnification electron micrograph cross section of the same sample as shown in Fig. 2.

The x-ray mask[7] was fabricated using a substrate of back-etched B-doped Si onto which a 6000-Å-thick gold layer was deposited to act as the absorber. The x-ray exposures were conducted on the IBM beam line for x-ray lithography using synchrotron radiation from the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The x rays are in the energy range of 1–1.8 keV. The characterization of the beam and other details describing the system are given elsewhere.[8] Grafting experiments were performed in a vacuum system designed so that solutions of purified monomer could be degassed in a reservoir and then siphoned directly into the reaction chamber without exposure to air. The monomer solution consisted of 10% (by volume) acrylic acid in water and was degassed by first solidifying the solution with liquid nitrogen and then allowing the temperature to slowly rise to room temperature at 10^{-6} Torr. The monomer was then introduced into the reaction chamber and kept at 60 ± 2 °C using a water bath. Care was taken to be sure that the irradiated wafer came in contact only with vapor and not with the monomer solution. The grafting reaction was allowed to proceed until the test pattern on the PMMA could be detected visually (10–30 min). Wafers coated with PMMA which had been grafted with acrylic acid were baked at 120 °C for 15 min, and developed in toluene at 40 °C for 5–10 min. X-ray exposures were performed over a dose range from 1 J/cm^2 to $\sim 1 \times 10^{-4}$ J/cm^2. The patterns were observed using a scanning electron microscope (SEM).

In Fig. 1 is shown a positive tone image of PMMA developed by conventional methods after x-ray exposure to 1 J/cm^2. The sensitivity enhancement of grafted PMMA (*in situ* polymerization) can be seen from the results given in Fig. 2 for which the x-ray dose was 1×10^{-3} J/cm^2. Notice that the grafted PMMA exhibits negative tone with features discernible at the 1-μm level. The grafting time in this case was 25 min. The grafted PMMA was developed for 10 min. A measurement of the spatial resolution as well as sensitivity enhancement can also be seen in the SEM photomicrograph given in Fig. 3 which shows a cross section of lines and spaces taken from a sample similar to the one shown in Fig. 2. We have also observed feature sizes down to 0.5 μm at a dose of 1×10^{-3} J/cm^2. Exposure of PMMA to dose levels of 10^{-1}–10^{-2} J/cm^2 with subsequent grafting yielded results comparable to those shown in Figs. 2 and 3. However, grafting times of only ~ 10 min were required at the higher doses. PMMA exposed to 1×10^{-4} J/cm^2 followed by a 1-h grafting time, still exhibits negative tone but the image is nonuniform and there is substantial loss of resist during development.

In conclusion, this study has shown that x-ray-induced grafting of acrylic acid to PMMA yields a minimum ehancement to 10^3 in sensitivity for submicron lithography. Chemical studies of acrylic acid grafted onto PMMA by electron beam irradiation were reported by Gazard *et al.*[2] and *e*-beam lithography by Liu *et al.*[4] Both studies reported a thousandfold enhancement in sensitivity. Thus, in our present work we have extended the phenomenon of enhanced sensitivity for acrylic acid grafted to PMMA to include x rays.

We wish to thank the staff at the NSLS for their cooperation in providing us with an x-ray source. We also wish to thank members of the IBM x-ray lithography group at Yorktown Heights for the use of the exposure system. The research of the RPI group was supported in part by the Semiconductor Research Corporation.

[1] W. M. Moreau, Opt. Eng. **22**, 181 (March/April 1983).

[2] M. Gazard, C. Duchesne, J. C. Dubois, and A. Chapiro, Polymer Eng. **20**, 1069 (1980).

[3] S. E. Bernacki and H. I. Smith, in *International Conference on Electron Ion Beam Scientific Technology*, 6th ed., edited by R. Bakish (Electrochemical Society, Princeton, New Jersey, 1974).

[4] W.-T. Liu, J. A. Moore, J. C. Corelli, M. Bourgeois, and A. J. Steckl, Electrochem. Soc. **83-2**, 331 (October 1983).

[5] A. Gupta, R. Liang, F. D. Tsay, and J. Moacamin, Macromolecules **13**, 1696 (1980).

[6] A. Chapiro, *Radiation Chemistry of Polymeric Systems* (Interscience, New York, 1962), Chap. XII.

[7] R. Acosta, X-ray Lithography and Applications of Soft X-rays to Technology, edited by A. D. Wilson; To appear in Proc. SPIE, **448** (1984).

[8] J. P. Silverman, R. P. Haelbich, W. D. Grobman, and J. M. Warlaumont, *Electron Beam, X-ray and Ion Beam Technology for Submicron Lithography II*, edited by P. D. Balis; Proc. SPIE **393**, 99 (1983).

A novel technique to fabricate GaInAsP/InP buried heterostructure laser diodes

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A chemical etching process to obtain a double heterostructure of InP-GaInAsP-InP with a very narrow active layer width is proposed in which three layers are etched preferentially. The quaternary layer works as the inner etching mask; the cladding layers above and below the active layer show reversed-mesa and normal-mesa shapes, respectively. The method is used to fabricate a buried heterostructure laser which lases at 1.3 μm on the *p*-type InP substrate. The fundamental lateral mode operation with threshold current as low as 15 mA is achieved with 0.8-μm active layer width.

PACS numbers: 42.55.Px, 73.40.Lq, 81.60. – j, 81.10.Fq

$Ga_xIn_{1-x}As_yP_{1-y}$/InP injection laser diodes are one of the most suitable light sources for optical communication systems, since at their lasing wavelengths (1.1–1.6 μm), absorption losses and the dispersion of the fiber are very low. Stable operation at single transverse and longitudinal modes with reasonable output power is the basic requirement for use as the active component in the system; in particular a laser diode (LD) operating at the fundamental transverse mode could be the most favorable light source. Various types of LD structures have been proposed which can fulfill this requirement with the help of index guiding.[1] In order to achieve fundamental lateral mode operation, the width of the active region should be narrower than 3 μm. Among various types of LD structures, the easiest method to obtain such a narrow width could be the etching of a wafer with a double heterostructure (DH).

In this letter a new method of fabricating DH wafers with a rather narrow active layer by means of preferential chemical etching is reported. The method is adapted to a buried heterostructure (BH) LD lasing at 1.3 μm on the *p*-type InP substrate.

First, a DH wafer was grown on a (100) oriented zinc-doped InP substrate ($p\sim4\times10^{18}$ cm^{-3}, *EPD* $\langle 5\times10^3$ cm^{-2}) using a conventional liquid phase epitaxy (LPE) technique with graphite slide boat under flowing H_2 gas. The substrate and doping impurities, Sn and Zn for *n* and *p* types, respectively, were put in the boat after dissolving source materials into In metals at 700 °C. The system was soaked at 620 °C