Photoelectrochemical etching of integral lenses on InGaAsP/InP light-emitting diodes

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A photoelectrochemical method has been developed for etching integral lenses on light-emitting diodes (LED's). An LED wafer is immersed in an electrolyte and biased at a potential at which the etch rate is directly proportional to light intensity. The image of a photomask is projected onto the surface of the wafer to produce a spatial variation of light intensity to etch the desired shape. The method has been used to etch spherical lenses on the *n*-InP substrates of InGaAsP/InP LED's. Extremely smooth surfaces are obtained for etch rates $\lesssim 0.5\,\mu$m/min. The resulting lensed LED's gave the theoretically expected improvement in the light coupled into an optical fiber, indicating that the scattering loss of the lenses was very small. The technique is compatible with the standard LED processing and the apparatus required is relatively simple.

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To efficiently couple the radiation from a light-emitting diode (LED) into an optical fiber it is necessary to use an appropriate lensing scheme.[1] Although a wide variety of lens configurations have been described in the literature, the simplest and potentially the most efficient are those in which a lens is formed in the LED material itself,[2] i.e., an integral lens. Previously such integral lenses have been formed by chemical etching[3,4] and ion milling[5] but were limited to certain shapes and focal lengths and generally also required a lens on the optical fiber for most efficient coupling.

In this letter a photoelectrochemical (PEC) method is described for etching lenses on LED's that has a number of important advantages over the previous methods. The rate of etching is controlled by the light intensity at the semiconductor surface. By projecting light onto the surface through a photomask that has an appropriate spatial variation of transmission, lenses of a variety of shapes can be formed. Lenses that are aligned to every LED on a wafer can be simultaneously etched in one operation. The technique is compatible with standard processing procedures and materials, requires relatively simple apparatus, and is carried out at room temperature.

The method has been applied to the formation of spherical lenses on the (100) S-InP ($n \approx 10^{18}$ cm^{-3}) substrates of 1.3-μm wavelength InGaAsP/InP double heterostructure LED's.[6,7] PEC etching results from a decomposition reaction induced by photogenerated minority carriers at the interface between the semiconductor and an electrolyte.[8] In this case the etching results from oxidative decomposition induced by photogenerated holes according to the reaction[9]

$$\mathrm{InP} + xh^{+} \rightarrow \mathrm{In(III)} + \mathrm{P(III)} + (6-x)e^{-}, \qquad (1)$$

where x is the number of photogenerated holes required, $(6-x)$ is the number of electrons injected into the conduction band by reaction intermediates, and the solvated forms of the oxidation products, In(III) and P(III), depend on the composition of the electrolyte and its pH.[10] For the reaction in Eq. (1) to proceed, the semiconductor must be biased positively with respect to the electrolyte to form a depletion region in the semiconductor. When this condition is met there is a relatively wide range of potentials over which the etch rate is independent of potential (plateau region) and directly proportional to light intensity. We found potentials in the range of $+0.1$ to $+0.4$ V vs a saturated calomel reference electrode to be safely within the limits of this plateau.[9] The electrolyte and the light intensity are chosen to give smooth etched surfaces and etch rates that are directly proportional to the light intensity.[9]

A projection system (shown in Fig. 1) to image the photomask onto the LED surface was used to produce the desired light intensity pattern. The mask was designed to produce spherical lenses. Its actual transmission function depends on the ratio of the minimum to the maximum transmission. This ratio should be as small as possible to minimize material removal. Constraints on the spatial variation of optical density that can be practically realized limit its smallness and a value of 0.1 was chosen as a reasonable compromise. Assuming uniform illumination and the maximum transmission to be one, the equation for the transmission T as a function of the radial position r on the mask then becomes

$$T(r)=\begin{cases} \dfrac{R-0.1\sqrt{R^2-(D/2)^2}-0.9\sqrt{R^2-M^2r^2}}{R-\sqrt{R^2-(D/2)^2}} & r<\dfrac{D}{2M} \\ 1 \qquad r>\dfrac{D}{2M}, \end{cases} \qquad (2)$$

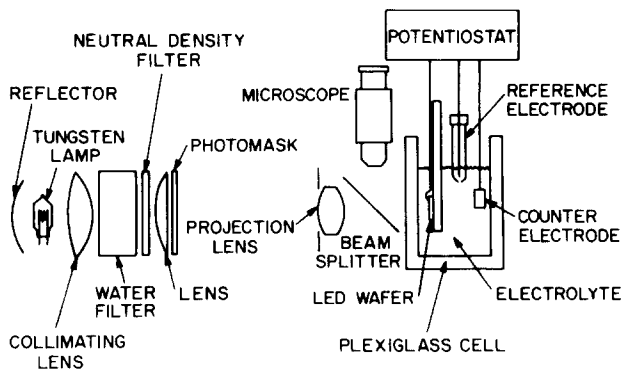

FIG. 1. Projection system for photoelectrochemically etching lenses.

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where R is the desired radius of curvature of the lens, D is the diameter of the lens in the plane of the substrate surface, and M is the magnification with which the mask is to be projected onto the surface. This will produce a spherical lens when the region surrounding the lens is etched to a depth of $\frac{10}{9}\left[R-\sqrt{R^2-(D/2)^2}\right]$.

Due to the difficulty of producing a precisely controllable continuous variation in optical density in an emulsion or other medium, a mask consisting of alternating transparent and opaque rings was fabricated. This also eliminates errors due to the wavelength dependence of the optical density of an emulsion. The radii of the rings were chosen so that the average transmission through adjacent pairs matched the desired transmission given by Eq. (2) at the boundary between the pair. The mask was fabricated by an electron beam exposure system (EBES) which produces the pattern in a chromium coated glass plate. In calculating the ring widths, the reflection of the glass ($\sim 8\%$) and the finite transmission of the chromium film ($\lesssim 0.5\%$) were neglected. The EBES system uses addresses at 0.25-μm intervals and a reasonably clean ring width of 1 μm can be achieved. With this minimum ring width, the mask was designed to be projected onto the surface with a magnification $M = 0.5$ and consisted of a 54×59 array of patterns. The magnification of 0.5 was chosen as a compromise between obtaining a smoothly varying light intensity on the LED surface from the ring pattern of the mask and being able to process as large a wafer as possible without having to step and repeat.

The mask was illuminated by a 100-W tungsten-halogen lamp using a condensing system consisting of an aspheric collimating lens, a water filter, and a lens to focus the filament onto the projection lens. A pellicle beam splitter between the projection lens and the cell directed reflected light from the wafer into a microscope to permit adjustment of the mask image. The cell, which was made of plexiglass, was mounted on a stage that allowed 3 translational and 3 rotational degrees of freedom. The orientation and transverse position of the cell were adjusted to align the wafer with respect to the mask image. The longitudinal positions of the lens and the cell were adjusted so that the magnification and focus were correct. A potentiostat was used to control the potential of the wafer and the current flow was measured to provide *in situ* monitoring of the etch rate.

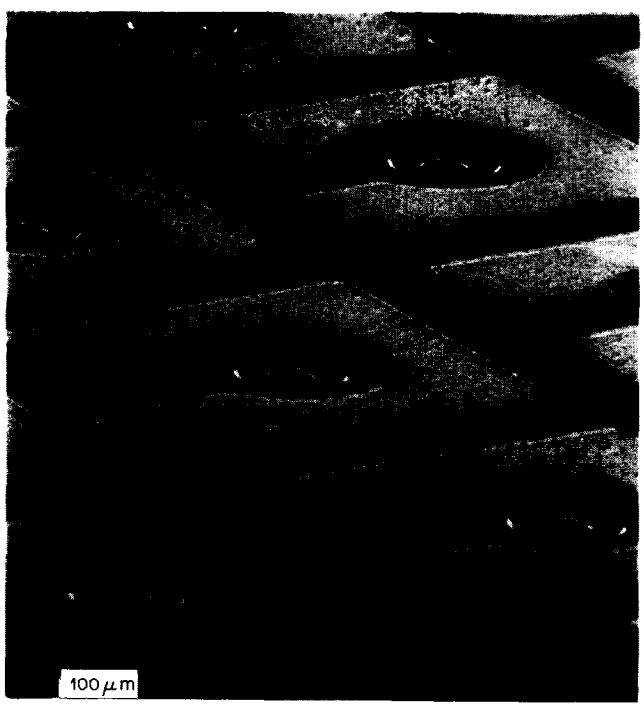

FIG. 2. Scanning electron photomicrograph of a section of an LED wafer with photoelectrochemically etched lenses.

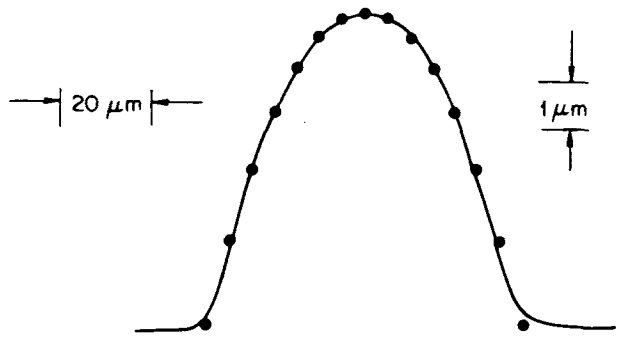

FIG. 3. Dektak surface profile of a lens (solid line) compared with a spherical profile (dots) having $R = 93\ \mu$m, $D = 70\ \mu$m, and a depth of 6.9 μm.

A scanning electron photomicrograph of a section of a wafer with lenses is shown in Fig. 2. There is no evidence of the ring structure of the mask on the lenses. Smoothing of the light intensity on the wafer can result from chromatic aberration of the projection lens (all $\lambda \lesssim 0.96\ \mu$m produces etching) and vibrations of the setup as well as the diffraction of the lens.

The lenses were etched to a height of 7 μm. To achieve this, the surrounding region had to be etched to a depth of 10 μm. This was consistent with a microphotometer measurement which gave a value of 0.14 for the ratio of the light intensity at the center to the surrounding region in the image of the lens spot but was greater than the value of 0.1 for which the mask was designed. This reduction in the contrast of the image could result from aberrations and scattering in the projection lens. The shape of the lenses was measured with a Dektak surface profiler. A profile taken through the center of a lens is shown in Fig. 3. The continuous line is the actual trace while the dots correspond to a spherical profile of radius of curvature 93 μm.

The power butt coupled into a graded-index optical fiber (core diameter = 62.5 μm, N.A. = 0.3) from LED's from the same wafer with and without lenses was measured. On average 60% more power was coupled from the lensed LED's. This improvement agreed to within experimental error with a calculated value based on a measured light spot diameter of 40 μm.[11] This indicates that the scattering loss of these lenses is very small.

A PEC method for etching integral lenses on InGaAsP/InP LED's has been demonstrated. Optically smooth lenses aligned to every LED on a wafer are simultaneously formed in one operation. All materials currently used in the standard processing of the InGaAsP/InP LED's are compatible with the method. Although the technique was demonstrated with spherical lenses, it is capable of pro-

ducing other shapes. In addition to InP, PEC etching of InGaAs, InGaAsP, GaAs, and GaAlAs has been demonstrated and is possible on all III-V semiconductors.

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[1]D. Marcuse, Bell Syst. Tech. J. **54**, 1507 (1975).
[2]O. Hasegawa, R. Namazu, M. Abe, and Y. Toyama, J. Appl. Phys. **51**, 30 (1980).
[3]Zh. I. Alferov, V. M. Andreev, B. V. Egorov, and A. V. Syrbu, Sov. Phys. Semicond. **11**, 1123 (1977).
[4]K. Iga, T. Kambayashi, K. Wakao, C. Kitahara, and K. Moriki, IEEE Trans. Electron Devices **ED-26**, 1227 (1979).
[5]O. Wada, S. Yamakoshi, M. Abe, Y. Nishitani, and T. Sakurai, IEEE J. Quantum Electron. **QE-17**, 174 (1981).
[6]H. Temkin, C. L. Zipfel, M. A. DiGiuseppe, A. K. Chin, V. G. Keramidas, and R. H. Saul, Bell Syst. Tech. J. **62**, 1 (1983).
[7]A. K. Chin, C. L. Zipfel, B. V. Dutt, M. A. DiGiuseppe, K. B. Bauers, and D. D. Roccasecca, Jpn. J. Appl. Phys. **20**, 1487 (1981).
[8]H. Gerischer and W. Mindt, Electrochimica Acta **13**, 1329 (1968).
[9]P. A. Kohl, C. Wolowodiuk, and F. W. Ostermayer, J. Electrochem. Soc. (to be published).
[10]S. M. Park and M. E. Barber, J. Electroanal. Chem. **99**, 67 (1979).
[11]R. H. Burton, F. W. Ostermayer, P. A. Kohl, C. L. Zipfel, J. A. Borsuk, C. Wolowodiuk, and I. Camlibel (unpublished).

New types of high efficiency solar cells based on *a*-Si

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Three types of new structure *a*-Si solar cells having more than 9% efficiency are presented. The first one has a high optical reflection back electrode metal alloyed with optically transparent *n*-type μc-Si deposited on the conventional glass substrate *a*-SiC/*a*-Si heterojunction solar cell. The second type structure is an inverted *p-i-n* solar cell having Ag/TiO_2/*a*-Si metal-insulator-semiconductor type back surface electrode which more efficiently collects longer wavelength photocarriers just above the band edge. The third structure demonstrated here has *a*-Si/polycrystalline tandem junction to pick up the energy of longer wavelength photons passing through the front side of the *a*-Si solar cell. All key technologies proposed here are practical and offer more promised real alternatives for the fabrication of high efficiency *a*-Si solar cells.

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In recent years, remarkable progress has been seen in both the physics and technology of *a*-Si (hydrogenated amorphous silicon) as a new electronic material.[1] Particularly, its significant properties (excellent photoconductivity with high optical absorption coefficient for visible light, the ability to produce a nonepitaxial growth on any foreign substrates such as glass, metals, and even plastic polymar films, and large area fabrication) make it a timely technology which matched with a strong social need for the development of a low cost solar photovoltaic system as a new energy resource.

Through wide varieties of recent research and development efforts with the aid of national or seminational projects,[2] the conversion efficiency of *a*-Si solar cell has been improved year by year as shown in Fig. 1. As can be seen from this figure, a steplike increase of the cell efficiencies is seen in the region 1981, while the slope A before 1981 corresponds to the improvement of the film quality and routine cell fabrication processes. The key technologies that produced the steep slope change from A to B at 1981, were the introduction of *a*-SiC:H (hydrogenated amorphous silicon carbide)[3] and *a*-SiGe:H (hydrogenated amorphous silicon germanium),[4] and also development of heterojunction solar cells with these new materials.[5] Owing to a recent advance of material synthesis technology by controlling the carbon fraction in $a\text{-}Si_{(1-x)}C_x$ (Ref. 6) and of the optimum design theory[7] based upon the concept of drift type photovoltaic process,[8] this type of heterojunction solar cell efficiency has continued to improve its efficiency with the slope B. The recent world record 10% efficiency by the RCA group in 1982 is also obtained in this type of *a*-SiC/*a*-Si heterojunction solar cell.[9]

One important remaining area for a further improvement of *a*-Si solar cell efficiency is more efficient collection of the longer wavelength photon's energy just above the band edge of *a*-Si, because the penetration depth of a 1.8-eV photon, for example, is the order of 5 μm,[10] while the thickness of an *a*-Si solar cell is only 0.6 μm. We have put our attention on this point, and conducted some attempts to pick up this region's photon energy. The purpose of this letter is to make a quick report on three practically promised results from the series of recent investigations with this aim.

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