Effect of laser-induced etching process on Porous structures

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Abstract

Various features of Silicon micro and nanostructures have been produced by lasers. Laser micromachining of silicon wafer has been conducted to fabricate devices for microelectronic circuits. The laser beam initiates a chemical reaction between the silicon and HF acid to synthesize porous layers by a laser-induced etching process. It is found that the etching rate increases for longer laser wavelengths when CW lasers are used and could also be used to drill micro holes in the silicon wafer when higher laser power densities are used. While Q-switched Nd:YAG laser could be employed to produce ordered nanostructures. It is found that laser parameters are adequate to produce and control the micro/nanostructure characteristics. The surface morphology investigation reveals formation of porous layers of various structures and different laser parameters were affected differently on the surface morphology. Moreover, the SEM statistics imply that high pore density of smaller average pores diameters of 3 μm are obtained when the HF concentration diluted to 30%. Furthermore, gratings of submicrons scale can be made when proper processing parameters are selected precisely. Experimental analysis has been carried out to characterize the microstructured surface using computer software.

Keywords: Silicon nanostructures, laser microtrimming, laser machining;

1. Introduction

Semiconductor and electronics industries have subjected to continuous development for last three decades. These improvements have in turn led to the more highly integrated and reliable circuits [1]. Semiconductor devices and circuits are formed in and on the surface of wafers of a semiconductor material, usually silicon by a process called device fabrication. The polished starting wafer come into

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fabrication with blank surface and exit with the surface covered with hundreds of micro component. The revolution from electronics to microelectronics has been driven primarily by the component size reduction. This decrease has been brought about by dramatic increases in the imaging process which is represented by lithography and the trend to multiple layers of conductors [2]. Crystalline silicon is the heart of electronic industries due to its superior properties but its role is limited in many other applications because of the indirect band gap property. Silicon nanostructures have completely different features compared with those of bulk crystalline silicon [3]. The silicon industry development has extended the ordinary lithography to the new generation lithography (NGL). This technology utilizes lasers to precede individual electronic element of basic patterning processes. Laser processing of silicon has activated the fabrication of three-dimensional structures in the micron and submicron scale for microelectronics devices. Recently, lasers have also found new applications in microstructuring technology. Device component size and the number of component in an IC are the two common trackers of IC development. Component dimensions are characterized by the smallest dimension in the design which is called the feature size and is usually expressed in micron or nanometers. Typically Nd – YAG laser has a dominant role in precision processing. However, pulse lasers operating in the UV region allow the production of even smaller micrometer or submicron structures. On the other hand, in medical applications, catheters with miniature wires and reducing features in integrated circuits technology are making an increasing use for laser processing. Nanotechnology is replacing the conventional UV light sources due to its inherent advantage of high processing velocity and higher resolution. The microprocessor size of the Pentium II was a 0.25 micron technology while for the current and future generations of microprocessors is in the range of 0.18, 0.15 and 0.13 micron [4].

Processing with the Nd-YAG laser having higher pulse repetition rate and short pulse width has various advantages over the conventional etching and electroforming techniques. Besides the conventional in the semiconductor industries, these techniques have recently been applied to fabricate various micro – optical components [5] and photonic band gap structures [6]. Photonic band gap structures exhibit frequency band where the electromagnetic wave is forbidden or cannot propagate. Thereby, lasers are becoming indispensable tools in the semiconductor manufacturing and micromachining industries.

Reducing dimensionality in silicon and semiconductors offers fascinating changes in electrical, optical mechanical and electronic properties of the material-based device and the electron mobility becomes very high in these devices. Porous silicon is a complex network of pores separated by thin walls in the nanometer range. The porous structure is classified into three categories; macroporous, mesoporous and nanoporous according to the pores diameters and dimensions [3]. Canham has firstly observed an intense photoluminescence at room temperature [5]. Porous silicon has triggered a great attention since its amazing features could be used for many applications [6,7]. Micromachining is used to fabricate small-scale mechanical devices that are integrated with conventional microelectronics. Macroporous silicon has been observed to be highly effective for micro and nanomachining such as micromachined devices include motors, cantilevers and a wide variety of sensors that are designed to sense temperature, IR and UV radiation, fluid flow or gas flow. Many of these structures are fabricated on free-standing membranes, structures that can be easily fabricated using porous silicon [8,9]. Moreover, deep straight holes could be sufficiently used for micro capacitors [10].

Laser-induced etching (LIE) of silicon is a relatively rare technique for creating silicon nanostructures [11] and has been investigated for many applications such as hologram application [12], and grating application [13], which were mainly passive optoelectronic devices. Recently photochemically etched silicon has been considered for possible active optoelectronic material. Generally, in this process a Si wafer is immersed in aqueous HF acid and irradiated with laser radiation of appropriate wavelength and
power density, electron – hole pairs are generated in the irradiated area and a depletion layer is formed. A chemical reaction takes place involving the photo generated holes and the fluorine ions.

Furthermore, hydrothermal processes were employed to synthesize porous structures of minerals and semiconductors. Chen et al. [14] for the first time presented the hydrothermal technique, for obtaining porous silicon.

In semiconductors, a large number of grating investigations have been performed for the following reasons. First, forced light scattering at laser – induced gratings allows the study of changes in optical material properties due to a variety of nonlinear optical mechanisms. The absorption and refractive index changes are important for applications in real – time holography, phase conjugation, optical bistability, optical grating and laser mode – locking. These applications are facilitated because semiconductors are fairly well understood materials available in excellent quality and their physical properties can be controlled by chemical or radiation treatment. Second, lasers – induced gratings in semiconductors are of interest in studying the mobility of electron and holes, especially their transport and decay parameters. These material properties are important for the fabrication and understanding of electronic and optoelectronic devices like transistors, photo detectors and laser [16].

Laser-induced periodic surface structures have been extensively investigated on different materials for over two decades using a wide variety of laser sources from low power CW laser to nanosecond [17,18] and femtosecond [19,20] in the wavelength range from 0.240 to 10.6 μm [21,22]. The formation of periodic structures or ripples on the surface of semiconductors is useful for the fabrication of gratings. Periodic or ripple structures have a variety of potential applications, where increased surface area is desired. Reactivity of the submicron and nanometer size ripple structures on the semiconductor surface would be enhanced drastically due to the large surface to volume ratio and the probability of dangling bonds on the surface [23].

Aim of this work is to utilize the laser-induced etching process to produce micro and nanostructured silicon of different features. The resultant micro and nanostructures could be employed in various electronic and optoelectronic applications.

2. Experimental Work

Commercially available n-type and p-type crystalline silicon with different resistivities of (1.5 - 4 Ω.cm) and (111) orientation were employed as substrates for the laser – induced etching process. The thicknesses of the wafers were nearly 500μm. Different laser wavelengths were employed to synthesize the micro and nanostructures. CW diode lasers of 405, 530, 650, 810 and 1060 nm wavelengths. While Q-switched Nd:YAG laser of 1.06 μm was used to produce ordered structure. The laser illuminated spot on the silicon wafer was visible to the naked eye when visible lasers are used while infrared laser could be pointed out by a visible indicator. The porous layer was locally formed on the illuminated area of the sample. Later on, samples were kept in a plastic container filled with ethanol to avoid oxidation of the surface. The illumination processes were conducted in HF acid of 30% concentration diluted with distilled water. The surface morphology of the laser-synthesized porous layer was extensively examined and analyzed by Scanning electron microscope (ZEISS 800) to investigate the nanostructure of the porous layer. We have also measured the laser-wafer interaction temperature by digital laser probe thermometer (Lutron 250).

3. Results and discussion

3.1. The porous structure
The porous structure produced by different laser wavelengths was subjected to extensive investigations:

**The etching rate:** The silicon wafer is inert when immersed in HF acid but a chemical reaction initiated by presence of holes at the silicon surface. These holes could be generated by different techniques such as absorption of the laser light in the laser – induced etching process. The etching rate of the laser induced etching process which is considered as an etching speed is affected by different parameters and is governed by the diffusion rate and drift velocities of holes to the surface [16]. We have studied the etching rate as a function of laser wavelength. It is found that longer laser wavelength has a higher etching rate and this could be attributed to the higher absorption coefficient. This absorption reach its maximum value (resonance absorption) when the laser photon energy is equal to the band gap energy of the silicon (1.12 eV). Table1 gives the etching rate for the employed laser wavelength. Moreover, effect of the laser power density has been also studied for the same irradiation time 15 minutes when n-type silicon wafer is used. We found that when a low laser power density (less than 3 W/cm2) is used, no porous layer was observed and the etching rate increases to about three times when the laser power increases to 20 W/cm2 and holes could be drilled in the wafer when higher laser power densities are used (more than 30 W/cm2) as will be discussed later. This is attributed to the number of the electron-hole pairs generated at higher laser power density. The localized temperature measurements reveal that the higher laser wavelength produces higher temperature due to the exothermic reactions. Fig.1 shows effect of different laser power densities on the etching rate and the generated temperature.

| Laser wavelength (nm) | The Etching Rate (µm/min) |
|-----------------------|---------------------------|
| 405                   | 0.8                       |
| 530                   | 1                         |
| 650                   | 1.4                       |
| 810                   | 1.7                       |
| 1064                  | 2.2                       |
The surface area: Silicon nanostructures have been widely used for different applications due to its electronic and optical properties where large area is needed [24]. The effects of various parameters on the surface area of the nanostructured surface like; the laser wavelength, irradiation time and the HF concentration. For the porous area prepared with a power density of 15 W/cm² and irradiated with 405 nm for 30 minutes, the obtained surface – volume ratio is (40 m²/cm³). While for the sample prepared by the laser of 514 nm wavelength and similar other conditions, the obtained surface area/volume ratio was 25 m²/cm³. Furthermore, increasing the employed laser wavelength to 810 nm leads to decreases the surface area to 15 m²/cm³. It is found that decreasing the wavelengths leads to increase the obtained surface area of the porous silicon structure due to the increment of pore/column numbers as well as decrease the pore dimensions.

Other Surface – Area calculations were studied on three samples prepared in different irradiation time. The obtained Surface-Area ratio for the sample prepared by 405 nm and 20 minutes irradiation time was found to be 20 m²/cm³. While increasing the irradiation time up to 25 minutes leads to increase the surface area to 36 m²/cm³. Moreover, when the irradiation time is increased up to 40 minutes, the surface area increases to 56 m²/cm³. Moreover, the surface area of the porous layer could be increased when using a photoelectrochemical etching. Visible laser used with wavelength of 405 nm to illuminate the silicon wafer during the electrochemical etching. It is found that the illumination during the electrochemical etching enhances the surface area of the porous structure to 75 m²/cm³ compared with 40 m²/cm³ for the laser-induced etching process.

The surface morphology: In the laser-induced (LIE) process, pore formation occurs only at the regions of charge carrier's accumulation and that means the LIE is a localized process. This step is followed by redistribution of charge carriers due to variations in the surface environment. These charge carriers accumulate in positions where Si atoms are removed thereby causing further chemical reaction.

Controlling the surface morphology of porous structure produced by laser-induced etching is of great interest since the surface area of the porous layer would determine the field of application. Fig.2 (a) shows the porous structure produced by a green CW laser at power density of 15 W/cm² and n-type silicon wafer and (b) the ordered porous structure produced by Q-switched Nd:YAG laser pulse on p-type silicon.
The Nd:YAG laser has a great effect on the silicon processing and that is due to the resonance absorption since the photon energy is equal to the silicon band gap energy. We have employed a Nd:YAG laser of various operational modes and different parameters. We found that this laser could synthesize a porous structure when a CW laser of low power density was used as shown in fig. 3(A) and the same laser has a capability of producing holes in the silicon wafer when high power density is used (more than 30 W/cm²) as shown in figure (3B). While Q-switched Nd:YAG laser could be employed to produce holes of controllable diameter and uniform circular shape (3C).
3.2. Dynamic grating

Fabrication of micrometer size laser-induced periodic surface structures on single crystalline silicon by photoelectrochemical etching illuminated with 810 nm has been studied. The irradiation of the silicon surface with a high penetration depth wavelength (810 nm) in silicon lead to form a deep periodic structure. The periodic structure on Si surface is shown in Fig. (4). Structures of micrometer periodicity and a maximum valley depth of (20 pm) are observed as shown in Fig.(4)(A). The absorption depth of 810 nm laser light in Si is approximately 12 pm and the observed ripple structure has a larger valley height. However, for diluted HF electrolyte, the valley depth increases significantly during the laser irradiation. This enhancement caused by large density of photo-induced charge carrier. Photoelectrochemical etching induced by the excited carriers provides a feedback mechanism that reinforces the laser-induced etching formation because the rate of etching is related to the density of excited carriers.

Moreover, two different regions are clearly observed with a regular step of (35 pm) and line width of (20 pm) corresponding to the image of the interference pattern as shown in Fig(4)(A). The surface plot in Fig. (4) (B) reveals that Si samples having an array of parallel walls perpendicular to the surface. The wall height is about 20 pm and average width 25 pm.

There is a noticeable difference in the morphology of the diffraction grating produced by LIE and PECE. Small size grating parameters are obtained and this could be contributed to the effect of production smaller nanocrystallites sized by shorter wavelengths.
Three dimensional surface of the PS structure is illustrated in Fig.(5)(a) and (b). Morphological differences in the structure are clearly observed between Fig. (4) and fig. (5).

Silicon microstructures produced by photoelectrochemical etching have also been studied. Figure (6) shows porous structures prepared by laser-assisted electrochemical etching (photoelectrochemical etching). Since the chemical reactions of the photoelectrochemical are very slow in nature, front side illumination Fig. 6(A) and backside illumination Fig. 6(B) were also studied. We found that backside illumination gives better results (large number of small pores) due to the migration of the photo-generated holes at the back side toward the accumulated holes from the external power supply at the front side. The migration time is quite enough for the dissolution of the silicon surface. Furthermore, it is found that illumination with short laser wavelength during the etching process produces very fine structure. Moreover, excessive etching was occurred when long irradiation time is used as shown in figure 6 (C) where the number of the pores are less than those of shorter illumination time.

![Fig.4. (A) Micrograph of n-type PS lateral produced by LIE process (B) the surface plot of the micro-grating](image1)

![Fig.5. (a)The top view of the high resolution scanning electron microscope of n-type PS structure produced by PECE process and (b) the surface plot of the porous layer](image2)
4. CONCLUSION

In this study porous structures of various morphology could be synthesized and controlled by laser-induced etching process. Pulsed Nd:YAG lasers are suitable to produce ordered microstructures in the silicon wafer due to exothermic reactions, while high power density CW laser could be employed to drill holes within the wafer. Higher laser power density increases the etching rate of the chemical reaction. Micro-grating of different features compared with those of laser-induced etching could be produced by photoelectrochemical etching (laser-assisted electrochemical etching). Finally, excessive etching is occurred when the etching process proceeds for a long time. The results of this project could be used in microelectronic and optoelectronic applications.
Acknowledgements

The author wants to introduce there thanks to Department Research & Development / The Iraqi Ministry of Higher Education and Scientific Researches, for their financial support.

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