Recent Progress in Semiconductor Properties Engineering by Ultrasonication

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Abstract: This work presents review of the recent patents and applied researches in the field of ultrasonic processing of the semiconductor materials and devices. The ultrasound demonstrates selective and, simultaneously, complex character of the effect on semiconductors. In contrast to the thermal or light energy, uniformly absorbed over semiconductor volume, the acoustic wave energy is mainly absorbed by the crystal lattice defects. The peculiarities of this interaction results in practical applications of the ultrasonication of semiconductors for electronic properties design. It was shown that US processing has found technological niche as supporting operation during ion implantation process and growth of semiconductors. The use of an inhomogeneous stress and piezoelectric harmonic potential produced by surface acoustic waves in low dimensional heterostructures to improves the efficiency of available optoelectronic and nanoelectronic devices as well as create new ones. The phenomenon of acoustic cavitation that underlies at the basis of such technological processes as cleaning and sonochemical synthesis is discussed separately.

Keywords: Ultrasound, semiconductor devices, gettering effect, acoustics cavitation, sonochemistry.

1. INTRODUCTION

Ultrasound (US) is now used extensively in mechanical engineering for bonding and manipulation in micromachines [1], for cleaning in electronic engineering and medical/pharmaceutical industries [2], for nondestructive control and measurement [3], for health diagnosis [4], food treatment [5], etc. Besides, ultrasound proved to be a useful technique for generating novel materials by the sonochemical synthesis [6]. All of these applications have propagation and interaction of acoustic waves with condensed matter (liquid or solid).

This paper represents recent achievements in the field of engineering of semiconductor's properties by ultrasonic processing. In order to get insight into the capabilities of the ultrasound in this field, it is necessary to point out the following. First of all, there are three different techniques to generate US vibration in semiconductors. The most addressed methods use ultrasonic sources such as either an external piezoelectric transducer or internal piezoelectric effect which cause direct generation of US vibrations in crystal [7]. Another approach is based on thermo-optical mechanism of elastic wave's generation [8]. In these techniques, US frequency f_{US} has to be carefully varied from 20 kHz to 20 MHz resulting in US wavelength variation from 10^{-1} m to 10^{-4} m and changing, in such a way, the character of this impact on the object of processing. It is worth to note also that, as a rule, acoustic intensity W_{US} at US processing does not exceed a few W·cm^{-2}. And only sometimes, at sonochemical synthesis, acoustic intensity can amount tens W·cm^{-2}.

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Along with this, the propagation of US vibrations in a solid is accompanied by the absorption of the acoustic wave's energy dissipating into heat. Besides, the object of processing is subjected to the alternate mechanical stress during propagation of US vibrations as well as the electrical polarization through piezoelectric effect. All these factors provide the complex effect on semiconductor properties during US processing.

Another feature of the acoustic wave's interaction with condensed matter is a selective character of US absorption. In contrast to the thermal or light energy, uniformly absorbed over semiconductor volume, the acoustic wave energy is mainly absorbed by the crystal lattice defects. The dominating mechanism of the phenomena stimulated by the US processing is tightly related to point defect gettering in semiconductors [9]. At that, the alternating stress induced by US vibrations provides a strain-gradient environment where the enhancement of the defect diffusion takes place. This is explained by the thermodynamic formalism, when the strains affect defect diffusivity and cause variation in the activation energy [10].

Mechanism of ultrasonically stimulated phenomena in semiconductor crystals with extended defects is related to interaction between acoustic waves and dislocations in the frame of the vibrating string model of Granato and Luecke [11]. As a result, defect structure transformation stimulates numerous phenomena, having a resonance character very often.

It should be noted that acoustic cavitation is the basis of US applications in the field of semiconductor manufacturing. It also consists in a selective absorption of US energy by oscillating bubbles, releasing stored energy during collapse within extremely short time. Heating and cooling rates of this process exceed 10^{10} K·s^{-1}. As a consequence, the chemical effect of ultrasound arises from an acoustic cavitation [6].

Thus, the ultrasonic technique demonstrates selective and, simultaneously, complex character of the effect on a condensed matter, a low power-consuming as well as a high level of feasibility at combination of the optimal US parameters such as power, duration, and frequency.

This paper aims to provide an overview of the fundamental and applied researches in the field of ultrasonic processing of the semiconductor materials and devices. It briefly covers the main concepts which are significant to the understanding of a strong potential of US technology to be utilized as a semiconductor properties engineering tool.

2. SEMICONDUCTOR PROPERTIES ENGINEERING

Numerous investigations deal with US processing of semiconductor materials [12-25]. The effect of the ultrasound has been successfully explored by various research groups for II-VI and III-V materials as well as for silicon, which is an industrial key material widely considered in micro- and nanoelectronic technology, optoelectronic devices, integrated circuits (ICs), *etc*.

The investigation of the effect of US processing on silicon was focused mainly on the modification of its transport properties, for example, - the minority carrier diffusion length in solar-grade polyclystalline silicon [12]. This critical parameter determines a poly-Si quality and reflects the concentration of metal impurities (Fe, Cu, Cr) dissolved in the crystal. US processing during 30 min at the frequency f_{US}=80 kHz and the amplitude of acoustic strain generated by a transducer ε_{US} = 10^{-6} brought a 2.7-times enhancement of diffusion length after sonication [12]. Similar results were obtained for Cz-Si wafers under US processing at MHz-frequency regime (f_{US}=0.8-5.5 MHz) [13], see Fig. (**1**). In addition to previous investigations, it was found that ultrasonically stimulated increase in the diffusion length L is characterized by a threshold at $W_{US} \approx 0.5$ W/cm^2 and saturation at higher US intensities (> 2 W/cm^2). Moreover, there is a pronounced hysteresis. The experimental data obtained were explained based on the model of a bistable acoustoactive recombination centers such as Cr–B, Fe–B, or Fe–Al pairs. In detail this model was discussed by recent review [9].

Ultrasonication of the porous Si with the purpose of modification of its luminescence properties was described in [14]. The increase of the photoluminescence (PL) intensity by a factor of 2–3 stimulated by kHz-frequency US processing has been observed, see Fig. (**2**). It was shown that long-time UST dramatically slows the aging process of the porous silicon. Mechanism consisted in the repopulation of the dangling bonds of silicon atoms stimulated by US processing was proposed.

Thus, ultrasonic processing offers an effective means for properties engineering in silicon. This statement can be confirmed by the following. It was proposed to apply the MHz-frequency ultrasonic treatment as a recovery tool in the devices characteristics of the γ-irradiated Si-based semiconductor structures [15-17]. Authors have shown that US processing of the γ-irradiated (the dose ranged from $5 \cdot 10^6$ rad to $5 \cdot 10^7$ rad) structures can help to reduce the number of localized states in a desired area of the electronic device by the ultrasonically activated process of the point defect diffusion.

One of the interesting observations of the ultrasonically stimulated properties engineering of the silicon-based structures was reported in [18-20]. UST applied during the implantation of Si in SiO_2 results in lower concentration of the suboxide states suggesting the formation of Si nanoclusters with a distinctly sharper nc-Si/SiO2 interface [18]. It was shown that *in situ* applied US vibrations of f_{US} = (5-9) MHz and W_{US} = 1 W·cm^{-2} lead to the lowering of the precipitation threshold of metal atoms and an increase of the precipitate

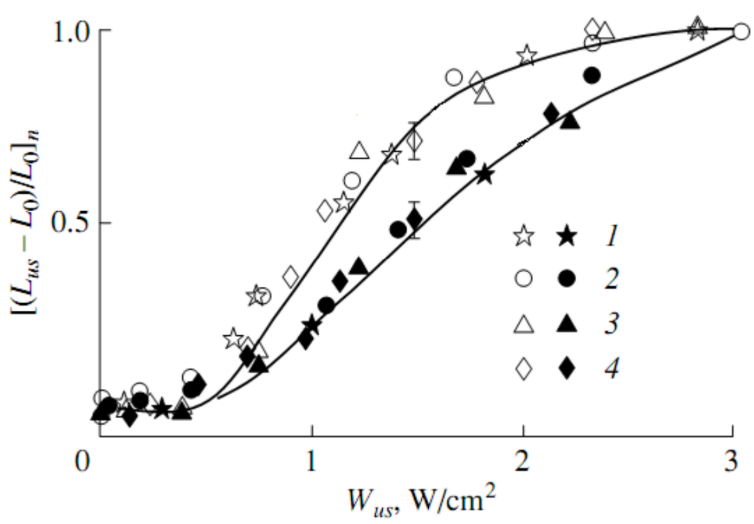


Fig. (1). Experimental data shows the dependence of the minority carrier diffusion length on the US intensity obtained for Cz-Si wafers: (1–3) - f_{US} = 0.78 MHz, (4) - f_{US} = 1.8 MHz. The data obtained in the initial and subsequent ultrasonic treatment cycles are represented by open and closed symbols, respectively. The ratio $[(L_{us} - L_0)/L_0]_n = 1$ corresponds to $(L_{us} - L_0)/L_0$ = (1) 1.2, (2) 1.15, (3) 0.95, and (4) 0.48 [13].

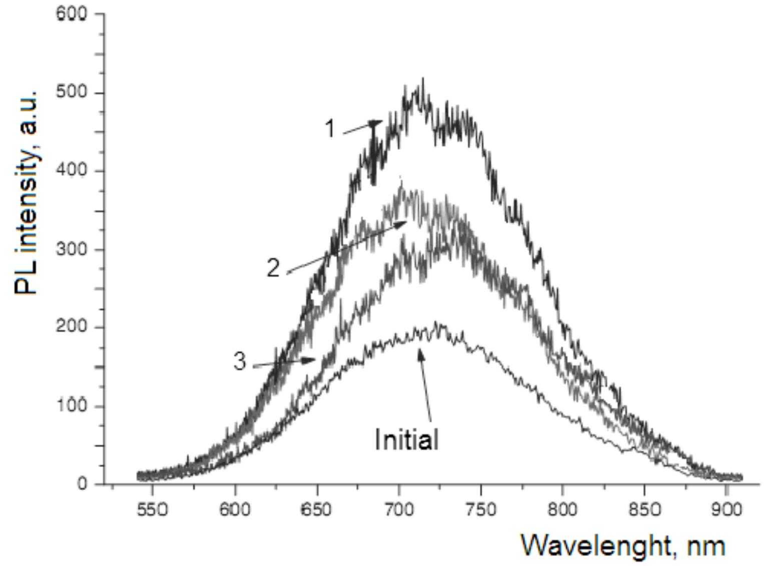


Fig. (2). Photoluminescence measurements as a function of the ultrasonic treatment (UST) duration *t* obtained for porous Si in [14]. Results show that there is an optimal time of UST to achieve maximal PL intensity (curve 1, t = 10 min). A longer UST time (curve 2 (t = 40 min), curve 3 (t = 160 min)) results in a suppression of this result.

size after post-implantation annealing of thermally grown SiO_2 [19, 20]. The samples of SiO_2 were implanted with 40 keV Ag^+ ions with dose $3{\cdot}10^{15}$ cm^{-2} [19] and 50 keV Cu ions at different doses (1-5)$\cdot10^{15}$ cm^{-2} [20]. The physical mechanism of this effect is attributed to the spatial redistribution of point defects and vacancy accumulation in the precipitation region.

According to the literature review, US processing has successfully been used to defect engineering in Si *p–n* junctions [21, 22]. The investigation of breakdown voltage of *p+–n* junction with reverse bias shows the increase of U_{bdv} by ~1.5 times with UST (f_{US} = 6 - 14 MHz and W_{US} = 0.2 - 0.5 W$\cdot$cm^{-2}) as shown in Fig. (**3**). The dislocation-engineered Si *p–n* junctions emitted the light even at room temperature were found to be sensitive to ultrasound treatment (f_{US} = 2.4 MHz and W_{US} = 1 W/cm^2) [22].

A systematic study on ultrasonically stimulated phenomena was carried out in mercury cadmium telluride alloys – the most widely used variable gap semiconductor for infrared photodetectors [23-26]. It was demonstrated that the action of the high-frequency (MHz) deformation excited by a piezo-transducer changes the carrier concentration up to the conductivity type conversion in HgCdTe epilayers [23]. It should be also noted that the negative differential resistance region was detected in the *I–V* characteristic measured in *n*-type HgCdTe bulk crystal during US processing (see Fig. (**4**)). The correlation between the density of extended defects and the value of the sonically

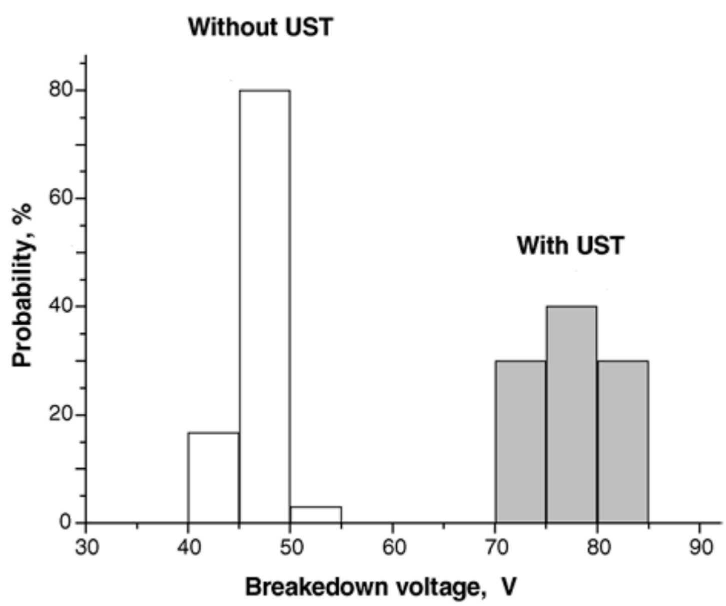


Fig. (3). Distributions of breakdown voltages (U_{bdv}) of reverse biased B-doped Si *p+–n* junction obtained by implantation without and with US processing [21].

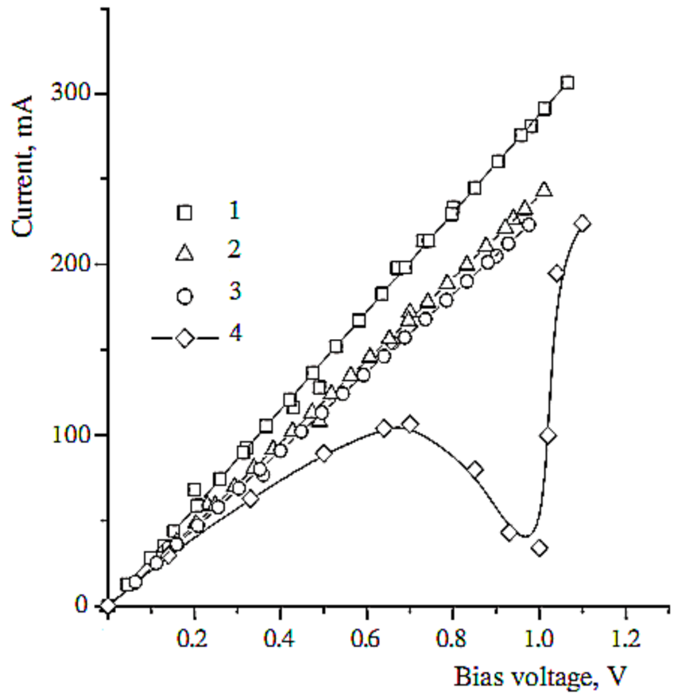


Fig. (4). *I–V* characteristics of the $Hg_{1-x}Cd_xTe$ bulk crystal at 78K with a negative differential resistance region. Results are obtained without US (curve 1) and with US (curve 2 - 4) at the amplitude of the electric field applied to the US transducer U_{US} = 6 V, 12 V, 15 V [23].

stimulated effects for bulk HgCdTe crystals has been found [24]. An ultrasonically stimulated thermal effect in $Hg_{0.8}Cd_{0.2}Te$ crystals was reported in [25]. Regions around dislocations heated during US processing were considered as sources of the infrared radiation, which can result in nonequilibrium carrier generation and changes in the electrical parameters of the material [26].

Thus, the observations described above exposes US processing as an attractive rout of the defect engineering opened the way for manipulating by electronic properties of the semiconductor structures and achieving of a stable improvement of electronic devices parameters. Let us consider some patents selected to demonstrate the possibility of using of US processing in semiconductor technology.

2.1. Selected Patents

First invention relates to US treatment of polycrystalline silicon thin films grown on glass substrates to enhance the process of hydrogenation and improve the electronic properties of such thin films [27]. A strong decrease of the sheet resistivity (see Fig. (**5**)) as well as improvement of the electrical homogeneity (see Fig. (**6**)) occurs after US processing of polycrystalline silicon. Spatially resolved photoluminescence and contact potential difference mapping confirmed

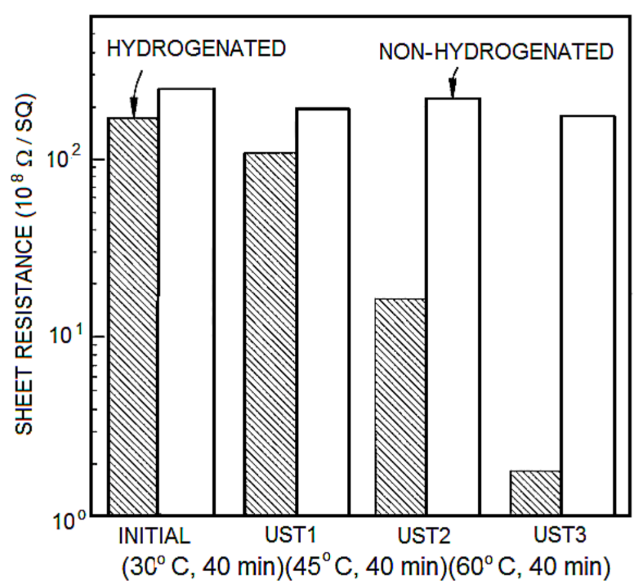


Fig. (5). The results of UST on sheet resistance of hydrogenated and non-hydrogenated samples. The hydrogenated sample demonstrates a dramatic one to two orders of magnitude decrease in resistance after UST [27].

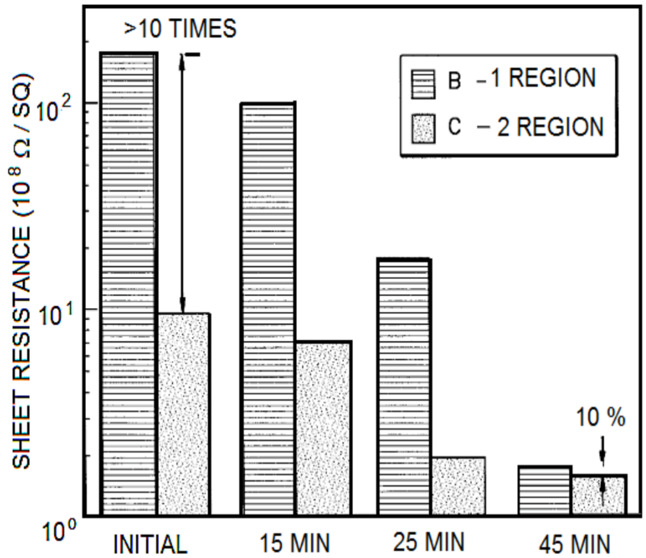


Fig. (6). Improvement of resistance homogeneity in hydrogenated poly-Si thin film versus time of UST; a comparison is given between the resistivity of two different regions of the same plasma hydrogenated sample [27].

that US effect is grain boundary related. Studies of hydrogenated poly-silicon thin-film transistors demonstrated remarkable improvement in transistor characteristics induced by US processing, especially, a reduction of leakage current by as much as one order of magnitude and a shift of the threshold voltage.

Next invention relates to utilizing US techniques to fabricating ion implanted semiconductor doping layers of an extremely shallow depth of penetration [28]. In accordance with National Technology Roadmap for semiconductors, depths of *p-n* junctions between 10 nm and 30 nm have been demanded for advanced highly ICs. For such shallow junctions, a lowering of the implantation energies during imbedding of the dopants into the semiconductor material as well as a reduction of the thermal budget in annealing the implanted profiles are required. In addition, the desired depth of penetration depends heavily upon the so-called transient enhanced diffusion (TED) influenced by non-balanced weight point defects that can be generated during the implantation process.

The invention [28] provides the suppression of the TED process by subjecting the semiconductor crystal, during the implantation process, to the effect of US oscillations at a power of between 50 W/m^2 and 10^4 W/m^2 in a frequency range between 0.01 MHz and 100 MHz. As a result, the altering depth and lateral distributions of the dopant impurities takes place (see Fig. (**7**)). The influence of *in situ* US processing at ion implantation on the basic parameters of shallow *p–n* junction has consisted in the increase of breakdown voltages and decrease of the leakage currents of *p+–n* and *n+–p* junctions. This point out the utilization of such processes can be beneficial for fabrication of high-performance semiconductor devices and ICs.

Invention [29] proposes to apply the US energy during ion implantation (or during a subsequent process, such as an annealing) for improving of the substrate cleaving. A layer of microbubbles is creates within a semiconductor substrate through the implantation of ions of a gaseous species, such as He or H_2. US processing causes smaller microbubbles to join together and reduces the straggle.

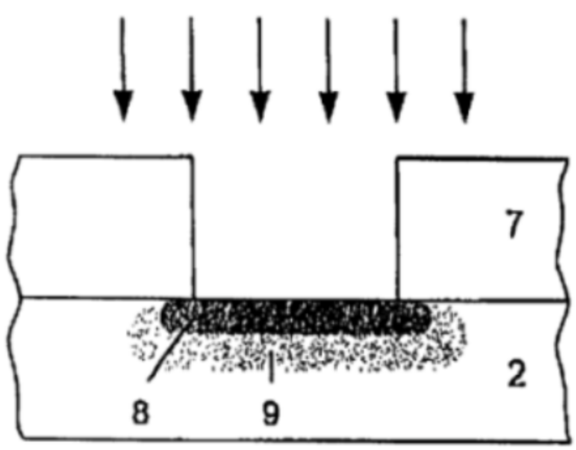


Fig. (7). Outline taken from [28] shows a section near the surface of the silicon wafer 2 with the implantation mask 7. The implanted area 8 is derived from ultrasonic treatment; the area 9 is derived without ultrasonic treatment.

It is necessary to point out some patents related to using of US vibration during growth process [30, 31]. In the former invention [30] it was proposed to input kHz-range US vibration energy acoustically coupled by a gaseous transmission medium into the solidifying (or cooling) material during solidification of the melt (or during subsequent further cooling) (see Fig. (**8**)). The expectation consists in the decreasing of the dislocation density in the solidifying (or cooling) multi-crystalline material. At the same time, it was found that the introduction of US vibrations of the kHz-frequency range into the source melt results in voids formation in the crystal related with the cavitation effect in the melt [32]. The eliminating of the striations in $Ga_xIn_{1-x}Sb$ as well as GaAs and InSb single crystals, obtained by Czochralski method, was achieved with high - frequency (1 MHz) *in situ* US processing [33].

The next invention [31] proposes a method for applying US vibrations (~70 kHz) to a wafer during the CVD (or PVD) deposition. Inventor claims that the applying of US vibrations allows the layer to deposit more conformal over opening sidewalls and decreases overhangs and voids.

Thus, the peculiarities of the interaction between ultrasonic waves and system of the point and extended defects in semiconductor crystal results in practical applications of the ultrasonication of semiconductors for electronic properties design. Moreover, US processing has found technological niche as supporting operation, especially during ion implantation process for the decrease of the activation energy of the point defects migration. The positive influence of ultrasound on the growth process is shown by the homogenization of the final product.

3. SURFACE ACOUSTIC WAVE DEVICES

Along with mentioned above, there is another opportunity to control and manipulate the properties of the semiconductor device through the use of the acoustic wave-inducing piezoelectric fields in heterostructures based on polar semiconductors. It concerns surface acoustic waves (SAW). The using an inhomogeneous stress and piezoelectric harmonic potential produced by ones for control of charge carrier transport and recombination in low dimensional heterostructures allows to improve the efficiency of available optoelectronic and nanoelectronic devices as well as create new ones.

In particular, surface acoustic waves (with frequency above 100 MHz and wavelength below 30μm) provide a way of introducing a dynamic one- or two-dimensional lateral modulation of the band structures of III-V quantum well structures which allows for dynamic control of the materials properties such as polarization anisotropy of photoluminescence spectra due to strain-induced band mixing [34], the ionization of photogenerated excitons [35] as well as carrier transport [36] and spin manipulation capability [37]. Recent advances and future prospects in the field of acoustically driven emission of light in layered semiconductors are reviewed in [38].

The Semiconductor Physics group at the Cavendish Laboratory (UK) has shown that a SAW pulse can be used to take an individual electron from one isolated quantum dot to another [39]. The principal idea of the experiment is shown and described in Fig. (**9**)**.** As think researchers, this may be useful for transferring quantum information between a quantum processor and its memory, or between parts of the same processor, using the electron's spin as a qubit.

SAW devices are used in electronic components to provide a number of different functions, including as delay lines, filters, correlators, dc converters, etc. SAW devices can be successfully used as biosensors, based on a biomolecules recognition system (see, for example, [40]). Such sensor is configured to detect minimum amounts of material through a principle in which the operation frequency or resonance frequency of the element is changed by a minute mass of a target which is introduced from the outside and captured by a detection layer on a surface of the element [41, 42].

It should be noted that progress in the field of the SAW devices developing for micro- and nanoelectronics requires a separate review. Hereafter we present a few selected patents indicating the SAW devices application in electronic circuits. The first invention [43] relates to a nitride-based semicon-

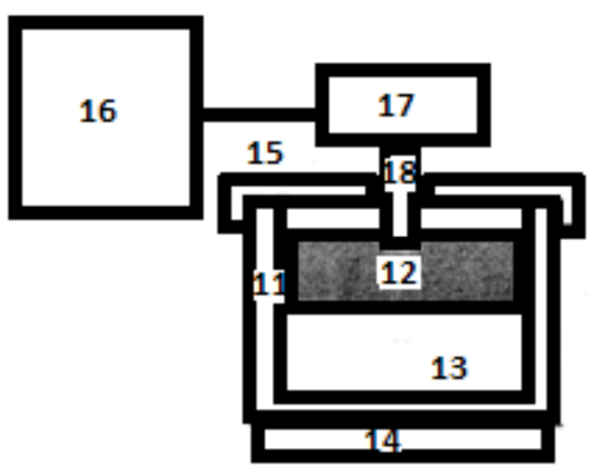
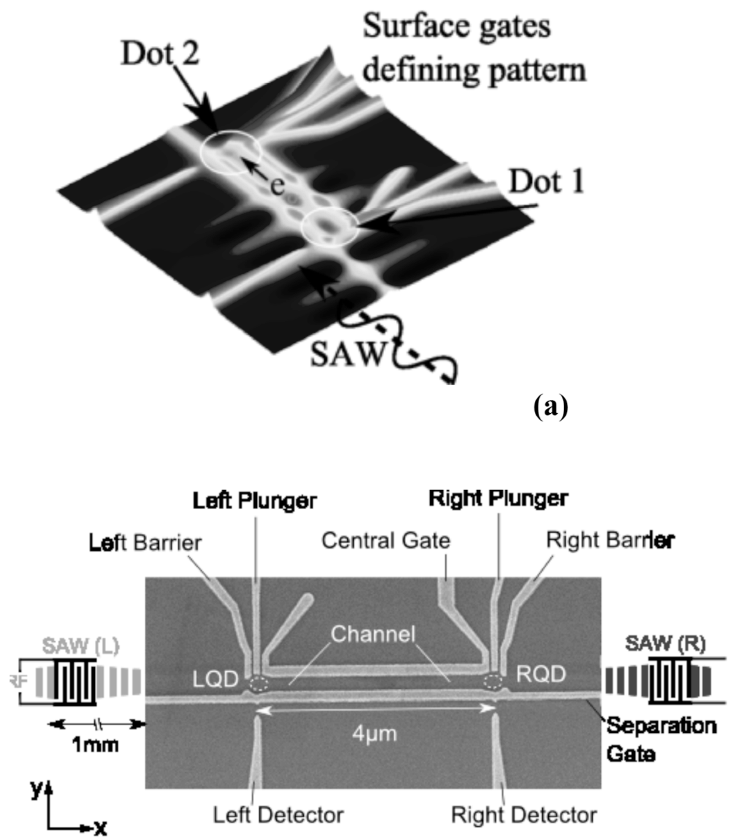


Fig. (8). Outline taken from [30] shows an application of the US vibration during solidification of the melt: 12 – Si-melt, 13 – crystallized Si-block, 14 – a cooling device, 11 – a graphite pot with the thermal insulation 15, 16 – US generator, 17 – US convertor, 18 – sonotrode (f_{US} from 10 to 25 kHz).

ductor device in which a heterostructure field effect transistor (HFET) and a SAW filter are integrated on a single substrate (see Fig. (**10**)). Since the GaN layer has a high surface-acoustic-wave velocity, superior temperature stability and polarization effects of piezoelectricity, it can be easily used for the fabrication of a band-pass filter which can be operated on the order of GHz or more.

Patents [44-46] relate to the tunable surface acoustic wave technology and propose monolithically integrated tunable SAW (MITSAW) devices based on acousto-electric and acousto-optic interaction between SAW and a two dimensional electron gas (2DEG) in a $ZnO/Mg_xZn_{1-x}O$ quantum well to tune acoustic velocity in the SAW delay line. Inventions provide a family of electronic and photonic devices



(b)

Fig. (9). SAW-driven transfer of an electron between distant quantum dots: (**a**) - the diagram shows the potential energy of an electron as a pulse of surface acoustic waves passes a quantum dot; (**b**) - Scanning electron micrograph of the device. Voltages applied to gates (light grey) create QDs (dashed circles) connected by 4 μm channel. Applying a microwave pulse to left/right transducer (placed 1 mm from device), generates SAW pulses, which trap and transport electrons. (www.sp.phy.cam.ac.uk).

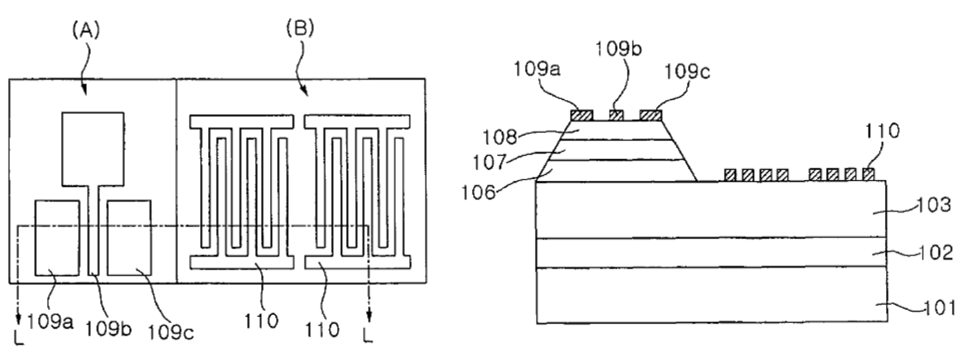


Fig. (10). HFET device proposed by [43] – top and lateral views. In the figure (**A**) denotes a region where an HFET is formed, and (**B**) denotes a region where a SAW filter is formed. An HFET consists of a drain electrode 109 a, a gate electrode 109 b, and a source electrode 109 c formed on the AlGaN layer 108 to accomplish an HFET structure. Semi-insulating GaN layer 103, which is formed on a substrate 101 includes a buffer layer 102, the Al-doped GaN layer 106 and the undoped GaN layer 107 preferably have a thickness ranging from 0.1 μm to 1 μm.

with improved operational characteristics and manufacturability. Fig. (**11**) is a schematic showing of a ZnO based monolithically integrated tunable SAW device of the inventions.

Very interesting invention [47] related to formation and manipulation of fully spin entangled electrons by apparatus comprising a static quantum dot located part way along a quantum wire, means for generating an electrostatic wave propagating along the quantum wire and means for adjusting the electrostatic potential of the quantum dot. The means for producing an electrostatic wave may be a SAW transducer arranged to generate a SAW propagating along the quantum wire (see Fig. (**12**)).

4. SEMICONDUCTOR PROCESSING BASED ON ACOUSTIC CAVITATION

The nature of the interaction between acoustic waves and semiconductors permits to manipulate by crystal fields for a stable improvement of the electronic devices as well as developing new ones. At the same time, the ultrasound application resources haven't been limited in this context. Then we shall focus our discussion on the phenomenon of acoustic cavitation that underlie at the basis of such technological processes as cleaning and sonochemical synthesis and through which semiconductor properties can be engineered also.

The phenomenon of cavitation has a threshold character and consists in generation, growth, and collapse of bubbles in the liquid (see Fig. (**13**)). For cavitation activation the acoustic waves must have enough amplitude to overcome the molecular bonding forces in the liquid. The completion phase of the cavitation – implosion, is very localized and transient with a temperature of 5000 K and a pressure of 1000 bar [6]. These extreme conditions result in the chemical effect of ultrasound.

Cavitation occurs over a very wide range of US frequencies, from tens of Hz to tens of MHz. The oscillating bubbles accumulate ultrasonic energy effectively while growing to a certain size. The maximum size of the bubble is inversely proportional to the applied US frequency. At this, the lower energy of the implosion corresponds to the smaller size of the bubble.

Another significant feature of the acoustic cavitation is an interaction with solid surface. On the basis of various theoretical studies and experimental data on cavitation-surface interaction, it is possible to assert that a general physical mechanism responsible for the effect of cavitation near solid

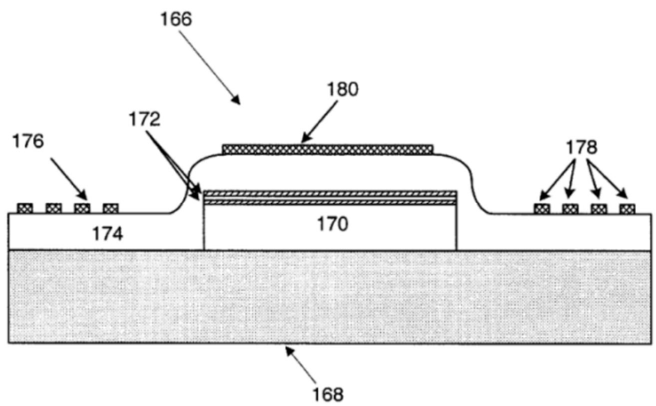


Fig. (11). Monolithically integrated tunable SAW device 166 of inventions [44-46] includes R-plane sapphire substrate 168, on which first ZnO layer 170 is centrally disposed. Quantum well structure 172 is disposed atop layer 170. Second ZnO layer 174 (piezoelectric) is disposed both on substrate 168 and on quantum well structure 172. Interdigital transducers 176 and 178 are disposed on second ZnO layer 174 as is electrode 180.

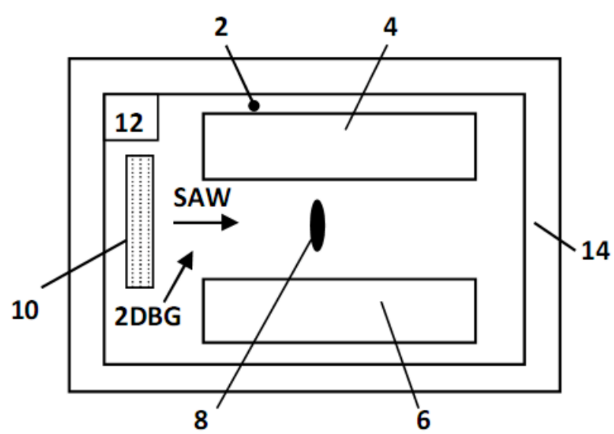


Fig. (12). A Gallium Arsenide semiconductor quantum well or heterojunction 2 is doped so as to form a two dimensional electron gas [47]. A quantum wire is formed by gate electrodes 4 and 6. Part way along the quantum wire a quantum dot is formed by gate electrode 8. A SAW transducer 10 arranged to induce a SAW propagating along the axis of the quantum wire is formed on semiconductor layers 2.

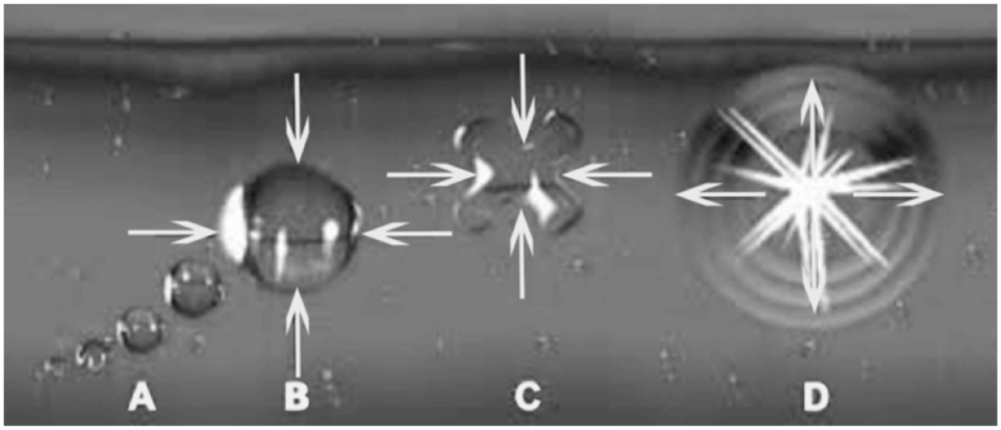


Fig. (13). Acoustic cavitation (from www.artios-tech.com): **A** – bubbles generation, **B** – bubbles growth, **C** - bubbles compressing, **D** - bubbles implosion.

surface is the micro-jet impact. The oscillating bubbles are asymmetrically imploded with the ejection of micro-jets of solvent at speeds of up to several hundred m/s. When bubbles expand and collapse close to boundaries, a shear flow is generated which is able to remove particles from the surface, thus locally cleaning it.

Thus, the above features determine the possibility of efficient use of cavitation to cleaning of electronic components as well as for the sonochemical synthesis of new electronic materials.

4.1. Ultrasonic Cleaning

Numerous cleaning methods, consisted in immersion in liquid cleaning agents to remove contamination through dissolution and chemical reaction, have been used in the manufacture of semiconductor electronic components. Brush scrubbing has been used to enhance the liquid immersion process. There are also methods involving pressurized water jet scrubs, rotating wafer scrubbers, wet chemical baths and rinses, etc. The addition of ultrasonic energy can increase the effectiveness of the liquid immersion process. So, high-frequency (> 40 kHz) ultrasound has been used in cleaning applications for decades [2].

Advances of the US cleaning are indisputable. Process of US cleaning is based on the phenomenon of the acoustic cavitation. Effectiveness and the amount of cavitation activity in the cleaning liquid strongly depends on the sonication conditions. First, there is a possibility of the destructive action of heterogeneous bubble nucleation at surface, i.e. cavitational erosion damage. Then, formation of standing waves in the ultrasonic tank at a fixed frequency can produce a harmonic vibration that damages delicate parts like electronic components. Moreover, the consequence of using systems with standing waves is inefficient cleaning. Smaller holes or detailed part areas may be missed, or receive only a small amount of cavitational activity. This is one of the most common complaints about single-frequency US cleaning systems.

Present-day inventions solve these problems. First of all, since the number of cavitating bubbles is directly proportional to the US frequency, whereas the average size of cavities is inversely proportional to the one, it is possible to adjust the cleaning intensity by the frequency control. A lower frequency (20–40 kHz) is suitable for heavy and coarse contaminants whereas frequencies of 60 to 80 kHz are recommended for delicate surfaces and 190–500 kHz US processing used for ultra-fine cleaning of semiconductor wafers [2].

To prevent the destructive effects of the cavitation megasonic cleaning is used [48] (see Fig. (**14**)). It operates at much higher frequencies, from 500 to 2000 kHz, and produces controlled acoustic cavitation. Unlike the violent implosion associated with kHz cavitation, controlled cavitation bubbles exhibit less violent collapse, producing lower temperatures and pressure [49]. Moreover, together with cavitation, effect of acoustic streaming cause particles to be removed from the material being cleaned. As a result, megasonic cleaning substantially minimizes surface erosion and damage to substrates being cleaned.

Patents [50-53] relate to the megasonic cleaning. Invention [50] proposes to optimize a wafer megasonic cleaning apparatus by adjustment of a pressure within the cleaning tank. At lower pressure, less acoustic energy is required to induce cavitation (see Fig. (**15**)). As pressure increases, a larger amount of acoustic energy is required to induce cavitation. Thus, controlling the pressure allows cavitation to be optimized and controlled about a particular acoustic energy.

Invention [51] proposes to use the frequency sweeping process for equalizing the megasonic energy generated by the transducers and improving performance of the cleaning. Inventions [52, 53] relate to the utilization of the multiple frequency regime of cleaning that reduces or eliminates standing waves within the liquid, resonances, high energy cavitation implosions, and non-uniform sound fields, each of which is undesirable for cleaning or processing semiconductor wafers and delicate parts (see Fig. **16**).

Cavitation activity can be significantly enhanced by applying pulsed sonication to gas supersaturated ultrapure water under traveling wave conditions [54].

In summary, it should be noted a huge number of patents dealing with ultrasonic cleaning equipment. So, US energy is now increasingly accepted by industry as an environmentally friendly, cost-effective, efficient, and safe means of the electronic components cleaning.

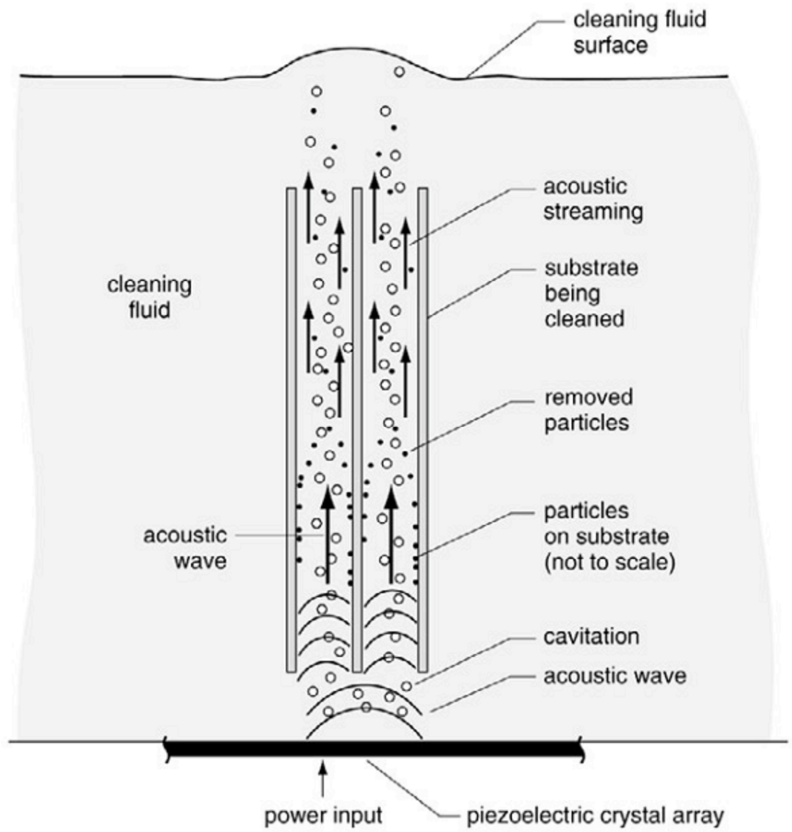


Fig. (14). An illustration of the megasonic cleaning process [48].

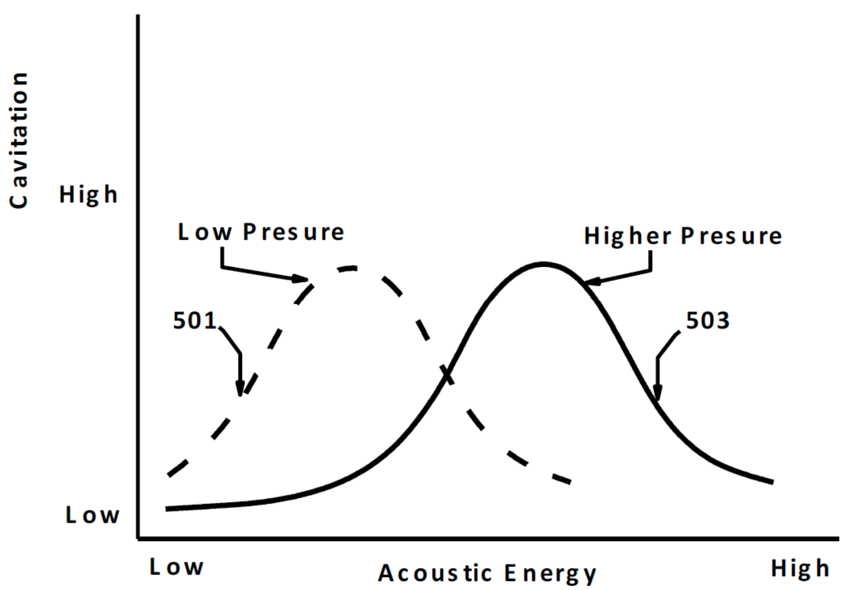


Fig. (15). A curve 501 illustrates this relationship between cavitation and acoustic energy. A curve 503 illustrates how the point of maximum cavitation moves toward a higher acoustic energy as pressure increases [50].

4.2. Sonochemistry

The chemical effect of the ultrasound is based on generation of free radicals during cavitation. Application of ultrasound to chemical synthesis allows accelerating a reaction or permitting use of less aggressive conditions, reducing the number of steps which are required using normal methodology, and opens the possibilities for alternative reaction pathways. Over the past decade, scientific interest in sonochemistry has considerably increased and focused on various topics such as preparation of nano-particles, porous and nanostructured materials, nucleation processes and semiconductor nanostructure synthesis *inter alia*. The application of ultrasound to materials science was discussed by early remark-

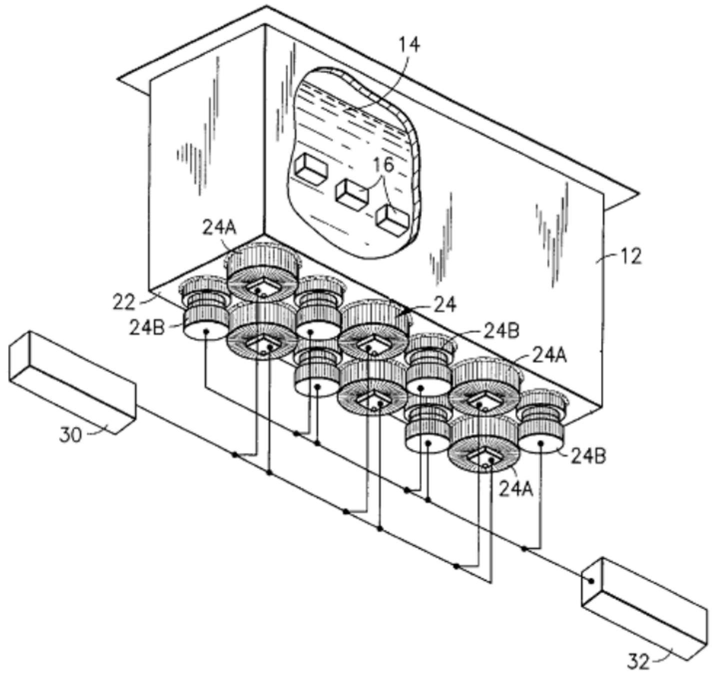


Fig. (16). Bottom perspective illustration of an US cleaning apparatus constructed for the multiple frequency regime of cleaning [53]. A cleaning tank 12 containing a cleaning bath 14 of US cleaning fluid within which there are immersed articles 16. Plurality of ultrasonic transducers 24 are affixed to the outer surface 22. Transducers 24A are powered by a first power supply 30 to provide US energy at a first f_{US}, and transducers 24B are powered by a second power supply 32 to provide US energy at a second f_{US} different from the first US frequency.

able reviews [6, 55, 56]. The goal of this chapter is to scan recent literature for semiconductor synthesized using US radiation.

The most studies in this field have focused on II-VI semiconductors - nanostructured chalcogenides especially (CdS, ZnS, PbS, CdSe, ZnSe, PbSe, *etc.*). The reason for their popularity is importance to non-linear optics, photovoltaic field, optoelectronics, and for such technological applications as biological labels, and electrochemical cells. A typical sonochemical synthesis of II-VI semiconductors involves the US irradiation of an aqueous solution of a metal salt and a chalcogen source [6].

The inventive method [57] for producing quantum dots (QDs) (CdSe Cores Synthesis from Cadmium Stearate) proposes the method of the synthesizing nano-crystal nuclei from a chalcogen-containing precursor and a precursor containing a group II or VI metal using an organic solvent. Ultrasonic treatment allows for higher disaggregation of QDs cores, which, in turn, causes more homogeneous growth of the shell.

In Ref. [58] several advantages of a sonochemical procedure over thermal synthesis were highlighted: better control over growth rate of nano-crystals via US intensity and significantly lower reaction temperatures. CdSe / ZnS core/ shell QDs were prepared by a two-step sonochemical process. They exhibit high photoluminescence, with quantum efficiency of 50–60% and a narrow size distribution of 10%. The corresponding invention describes the fast low-temperature synthesis of quantum dots, such as CdTe or CdSe, via thermal and sonochemical methods [59].

A new method to synthesize CdS nano-particles at a relatively low temperature (60° C), short time, and fast transition phase through combination of US waves and micro-emulsion was proposed in [60]. The advantages of this combined method are due to its simplicity and efficient way for preparation of nano-particles with uniform shape. Equally well, CdS–TiO_2 core–shell nano-composites were synthesized at low-temperature (~70° C) through a combination of ultrasound and micro-emulsion without surfactant [61].

Sonochemical synthesis of metal oxides with semiconductor properties has also received interest due to their technological importance. Examples of successful explorations include TiO_2 (3.2 eV band gap) [62], nanocrystalline NiO powder (4.3 eV band gap) [63], CuO (1.2 eV band gap) [64], Mn_3O_4 [65], and others.

Ref. [66] describes a technique to prepare vertically aligned ZnO nanorods that have interesting potential applications to solar energy conversion (see Fig. (**17a**)). In this work, US irradiation rapidly induced anisotropic growth of ZnO along the (0001) direction on various substrates (e.g., Zn sheet, Si-wafer, glass, and polycarbonate). Compared to conventional approaches, such as a hydrothermal method, the growth rate of ZnO was increased more than tenfold, with an average growth rate of 500 nm h^{-1}.

The shape of the semiconductor nano-structure obtained by the sonochemical method can be controlled by various sonication conditions, including US duration. For example, it was found that uniform ZnO nano-rods with diameter around 50 nm were formed after 15 min of ultrasonication while flower like ZnO nano-structure was formed after 30min (see Fig. (**17b, c**)) [67]. Variation of the reducing agent at sono-

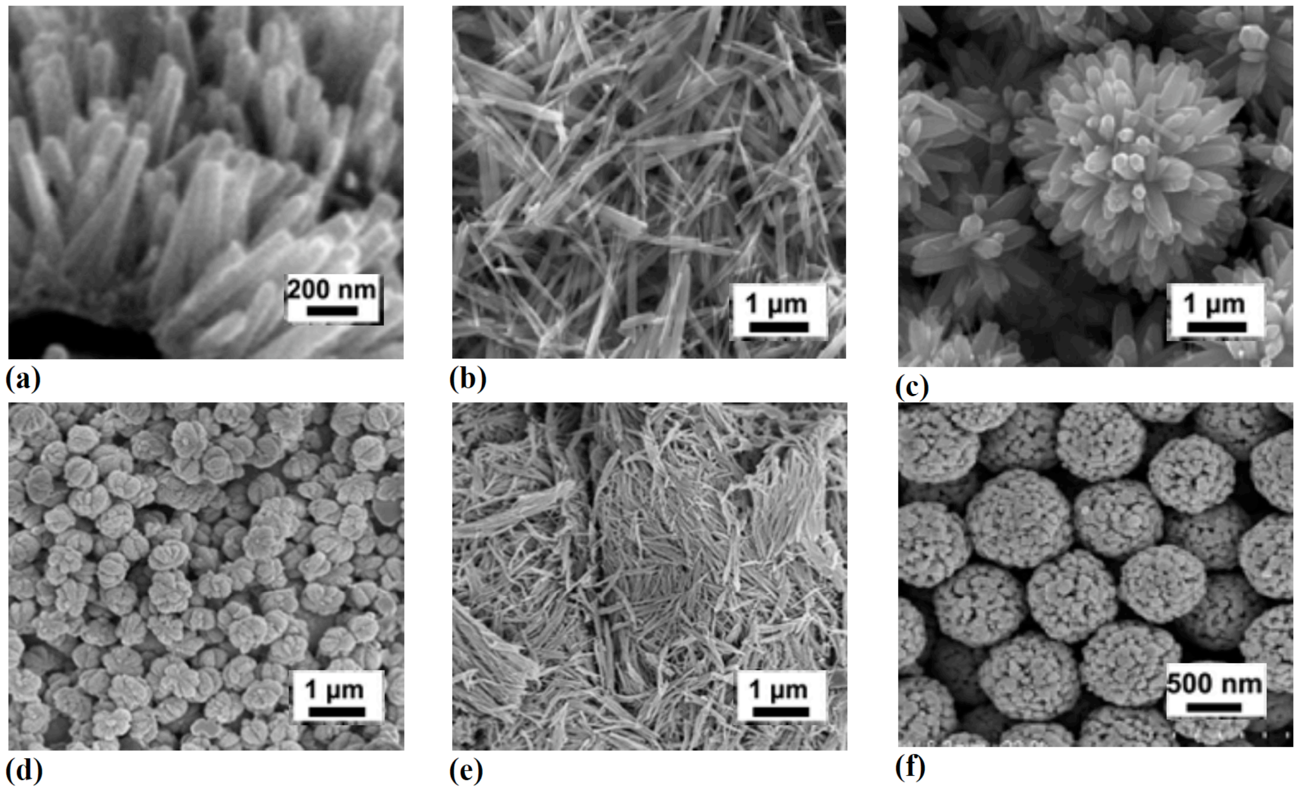


Fig. (17). Examples of the sonochemically synthesized semiconductor nanostructures: **(a) -** aligned ZnO nanorods on a substrate [66]; **(b) -** ZnO nano-rods and **(c) -** flower like ZnO nano-structures [67]; **(d)** – CuO nanostructure using urea as reducing agent, **(e)** – CuO nanostructure using sodium hydroxide as reducing agent [64]; **(f) -** porous Cu_2O nanospheres prepared by using ascorbic acid as the reducing agent and β-CD as the capping agent [68].

chemical synthesis permits to change the morphology of the reaction product also (see Fig. (**17d, e**) [64].

A simple, rapid, economic and environmentally friendly method for the synthesis of porous Cu_2O nanospheres, which is promising applications in many fields, such as solar energy conversion, gas sensing, and lithium ion batteries, has been developed via a sonochemical route [68] (see Fig. **17f**). Porous nanostructures are exceptionally useful in sensing, catalytic, and mechanical applications because of their high surface area, tunable pore size, and adjustable framework.

A number of investigations deal with sonochemical synthesis of III-V compounds. In particular, nanocrystalline InP [69] and GaSb [70] were obtained by this rout. Invention [71] represents a method of synthesizing a III-V binary alloy nano-particle. Said methodology comprises the use of reductive sonochemical methods to generate reactive species *in situ* resulted in the formation of a desired product. This patented method was applied to the preparation of MP (M = Ga, In) nanocrystalline materials [72]. Synthesis at low reaction temperatures with a relatively short reaction time and the reduction or elimination of unwanted side reactions was claimed.

Thus, it should be noted that sonochemical synthesis in liquid precursor is found to be superior to traditional methods in the production of high-quality semiconductor nanostructures.

The extreme value of the temperature and pressure arising in cavitating liquid during bubbles collapse close to the solid surface can damage it locally forming various surface structures. US modification of solids is known to be controlled by various sonication conditions, including the frequency and duration of sonication [73, 74]. The formation of channel-like structures was observed in silicon samples prepared by 10 min of sonication at 20 kHz (Fig. **18a**). Samples modified for 20 min reveal partial surface amorphization (Fig. **18b**), which later converts into a completely amorphous microporous silicon structure (Fig. **18c**). The exposure of Si substrate to megasonic cavitation obtained by focusing a high frequency (6 MHz) acoustic wave in cryogenic liquid results in the creation of the dendritic objects inside ultrasonically structured region (see Fig. **19**). Array of microstructures was successfully formed on the surface of GaAs using processing it in cavitating cryogenic liquid [75].

At the same time, the behavior of semiconductor surface under acoustic cavitation remains not well addressed. Possible application of acoustic cavitation for material deposition from solution on semiconductor surface was presented in [76]. The method of a combination of US waves and microwave irradiation for generating plasma and thin films deposition (such as an amorphous carbon film and a silicon carbide film) was described and patented in [77]. The deposition of nano-structured materials by means of a plasma arc discharge obtained in an acoustic cavitation field has been reported [78-80].

A few works describe the sonication of crystalline Si at 20 kHz and the change of the physical, chemical, and struc-

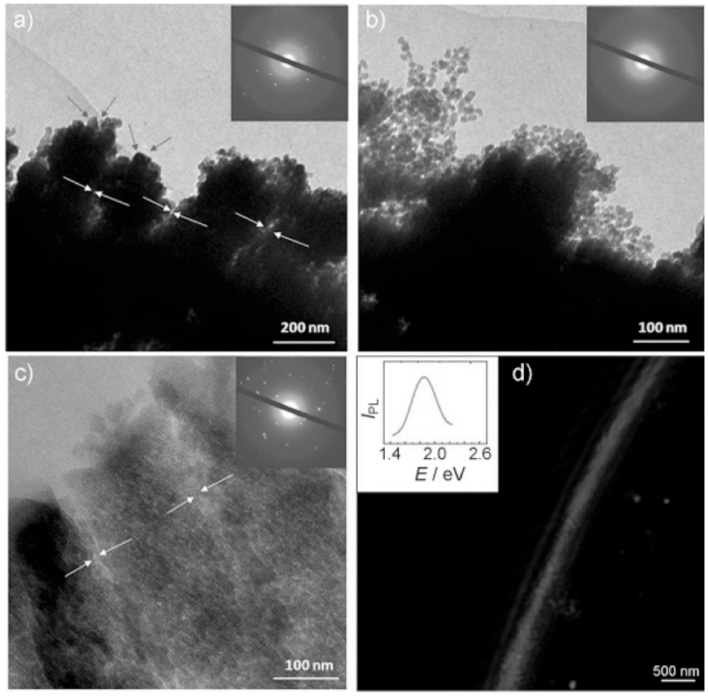


Fig. (18). TEM images of the US (f_{US}=20 kHz) modified silicon wafer in aqueous solution after (a) 10 min, (b) 20 min, and (c) 30 min of modification. Insets (a–c) show electron-diffraction patterns of the samples modified for the corresponding time; (d) μ - confocal photoluminescence spectra of the Si after 30 min of modification [74].

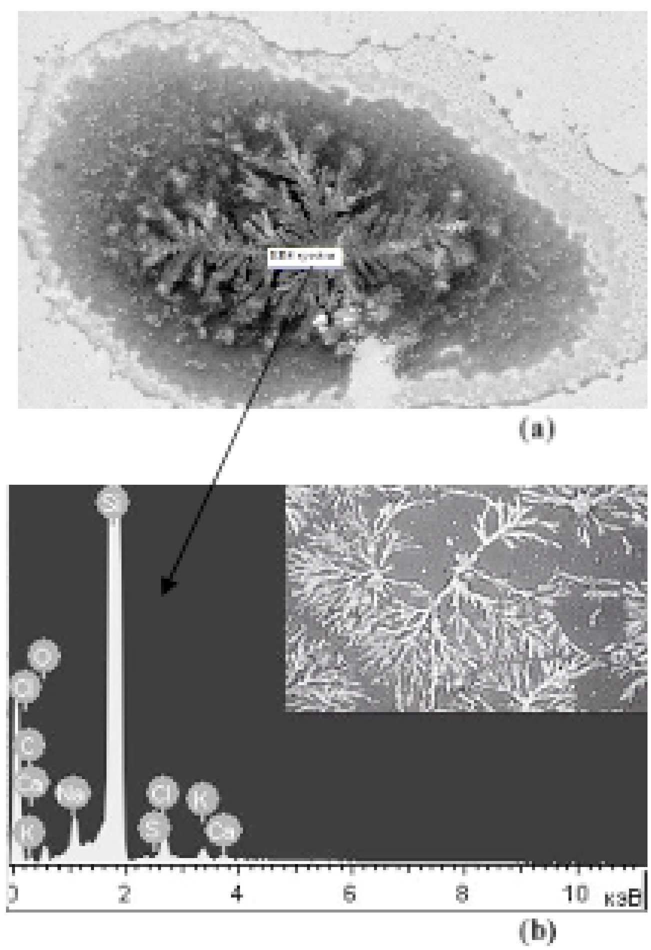


Fig. (19). SEM micrograph **(a)** and the atomic composition of the structured silicon surface **(b)** exposed to the acoustic cavitation in liquid nitrogen at 6 MHz during 15 min. Inset: an optical image of silicon surface exposed to the acoustic cavitation during 1 hour [73].

tural properties of this semiconductor. Phase transformations of the Si lattice have been observed by Raman spectroscopy evidencing the complex stress state induced by acoustic cavitation in the Si crystal structure [81]. The effects of microbubble cavitation close to silicon surfaces have been described in [82]. Different erosion evolution was observed for (100), (110), and (111) Si surfaces, exposed to cavitation bubbles generated by US signal of 191 kHz after 180 min sonication. (100) Si substrates showed the most erosion damage.

Ref. [74] has demonstrated the porous silicon formation with unique optical properties through a "green" method of ultrasonication. The method for modifying the structural properties of silicon by ultrasonication in the presence of a liquid HF-free medium is patented in [83]. The frequency of the sonochemical process was constant 20 kHz, whereas the intensity of US exposure was varied from 7 to 57 W/cm^2. The duration of sonication was also varied from 1 min to 90 min.

The exposure of GaAs substrate to megasonic cavitation obtained by focusing a high frequency (3 MHz) acoustic wave into liquid nitrogen and the phenomenon of the nitrogen atoms incorporation into GaAs lattice with Ga-N bond formation in the region of the maximal structural change due to the cavitation impact was described [84].

CURRENT & FUTURE DEVELOPMENTS

In conclusions, the review of the applied researches and recent patents in the field of ultrasonic processing of the semiconductor materials and devices has demonstrated a strong potential for the US technology to be utilized as a semiconductor properties engineering tool. The physical origin of the US effects on a semiconductor is connected with interaction between acoustic waves and crystal lattice defects. Another opportunity to control and manipulate the semiconductor properties consists in the use of the acoustic wave-inducing piezoelectric fields. Such interaction results in an effective transformation of the absorbed US energy into the internal vibration states of the crystal stimulating numerous defect reactions and semiconductor properties engineering. It would like to mention separately the opportunity to control and manipulate the properties of the semiconductor device through the use of the surface acoustic wave.

Ultrasonic processing has found technological niche as supporting operation during the electronic device manufacturing. There can be mentioned structure growth, properties engineering by the ion implantation and post-implantation annealing as well as such procedure as bonding, cleaving and properties monitoring. Ultrasonic cleaning technology, which is in a state of change and development, should be noted especially.

From the literature review, it was identified a number of possible avenues for further research and development in the field of ultrasonic application for semiconductor properties engineering. It is obvious, future progress of ultrasonic technology is connected with sonochemistry advances. Sonochemical synthesis is found to be efficient for the preparation of semiconductor nanostructures at room temperature and atmosphere pressure. The successful and challenging collaboration between US and microwaves techniques should be noted especially. It is necessary to underline also that the sonochemistry of solids could open fresh prospects in the area of novel "green" method development for semiconductor properties construction.

CONFLICT OF INTEREST

Here, I stated that no financial contributions to the work were received, and no patents in various stages of legal litigation were cited.

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