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# 3D periodic structures grown on silicon by radiation of a pulsed Nd: YAG laser and their field emission properties

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## Abstract

Periodic three-dimensional structures were successfully grown on single crystal Si wafers either bare or Au-covered under their exposure to a pulsed radiation of a Nd:YAG laser in vacuum. The structures protrude above the initial wafer surface for 10 μm while their spatial period is about 70 μm. The coupling of the laser radiation to Si surface is related to the thermal non-linear absorption of the near band gap radiation. The structures exhibit an efficient field emission with an average emission current of 5 mA/cm$^2$ and is sensitive to the post-treatment of samples. The drawbacks of the emission current densities are discussed.


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*Keywords:* Laser ablation; Periodic structures; Field emission

## 1. Introduction

Three-dimensional (3D) periodic structures that arise on solids under ablation of multiple laser pulses are extensively explored after the pioneer work of Morenza et al. [1]. Apart from physical mechanisms of their formation [2–9], these structures are of interest for their potential applications as, e.g., a model of a black body emitter [10,11]. Three-dimensional structures on Si are of special interest since Si is the most common material in many electronic devices. Periodic micro-cones (micro-cones array, MCA) on Si show the ability for low-threshold field emission of electrons. Only two groups succeeded in observation of MCA field emission so far [12–15]. The turn-on field of cold electron emission of Si MCA is around 1 V/μm, which is comparable with the characteristics of electron emitters based on carbon nanotubes. The incorporation of nanotubes into MCA arrays on Si has been reported recently [14]. The aim of the present work is to study the influence of a metallic (Au) incorporation into MCA on Si on their field emission properties.

Till now MCA on Si have been generated using lasers photons with energy exceeding the bandgap of this material. As a consequence, this radiation was absorbed by a superficial layer of the crystal. In the present work for the first time use an infrared Nd:YAG laser (wavelength of 1.06 μm) for generation of MCA on Si. The sample is transparent at this wavelength, at least for weak laser fluence. The absorption of laser radiation and eventual melting of Si surface is achieved due to thermal generation of free carriers in the conduction band of Si. Au film used in this work is thin compared to laser wavelength and does not alter the absorption of laser radiation by the sample, which allows studying its influence on field emission. Also, a commercially available Nd:YAG laser is used for generation of MCA on Si instead of expensive laser sources, such as an excimer lasers or a Cu vapor laser, which is attractive for large-scale fabrication of inexpensive field emitters.

## 2. Experimental

Single-crystal Si plates were used for generation of 3D arrays of micro-cones. They were used either as received or with a 30-nm Au film deposited on it via sputtering. The details

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of the experimental setup used for generation of MCA are described elsewhere [7–9]. Briefly, the samples were placed into a vacuum cell with a glass window and pumped out to residual air pressure of 1 Pa. The cell was mounted on a computer-driven *X–Y* stage allowing the displacement of the sample under a laser beam focused on it through the window. The scanning velocity and the overlap between consecutive scans allowed varying the number of laser shots delivered to a given point of the sample. Typical dimensions of the laser-treated area were about 1 $cm^2$. A pulsed Nd:YAG laser was used for irradiation of the samples operating at wavelength of 1.06 μm with pulse width of 130 ns and repetition rate from 1 to 5 kHz. The Si samples were transparent at low fluence of the laser beam, so a ceramic holder was used to avoid laser heating of the back side of the sample. The cell with the sample was continuously pumped out during the process of laser irradiation. The samples were characterized by a scanning electron microscopy (SEM), either as prepared or treated in an aqueous solution of HF after laser irradiation. Field emission characteristics of the MCA were studied in a high vacuum chamber with a pressure below $10^{-5}$ Pa. The voltage was applied between a flat-ended tungsten tip and the film surface, with the tip-surface distance being varied between 10 and 100 μm. An XYZ stepper motor stage is used to control the tip motion in three directions. An optical telescope system with a CCD camera and monitor are used for monitoring tip positioning, and for immediate in situ observation of any electrical field induced modification of the sample surface. A high dc voltage, up to 8 kV, is applied between the sample and the probe to induce field emission. The measurement procedure included recording of the emission current during the automated cycling of applied electrical fields. The emission current density was calculated by dividing the measured current by the total surface area of the used tip, which is about 0.25 $mm^2$. The turn-on electrical field and the emitted current density were measured for several MCA samples laser generated under different conditions. Alternatively, the emission current was measured using a flat screen placed over the sample surface at distance of 200 μm. The image of the emitting area was recorded using a CCD camera allowing direct observation of distribution of the emission current over laser-processed area. The *I–V* characteristics were measured using the total emission current from the sample.

## 3. Results and discussions

Si samples are virtually transparent at wavelength of 1.06 μm, so the formation of periodic structures commences at some threshold laser fluence at about 20 J/$cm^2$. Unlike the growth of Si micro-cones under ablation with a Cu vapor laser [7–9], the formation of Si under a Nd:YAG irradiation starts from rather uneven surface relief (Fig. 1(a)). Typical number of laser shots needed for MCA formation in present experimental conditions is about 3000. The surface of the sample is covered by regular cracks and is also modulated by "waves" whose orientation is not related to the direction of scanning of the laser beam. Note that the increase of the number of laser shots does not change the observed morphology; it depends mostly on the

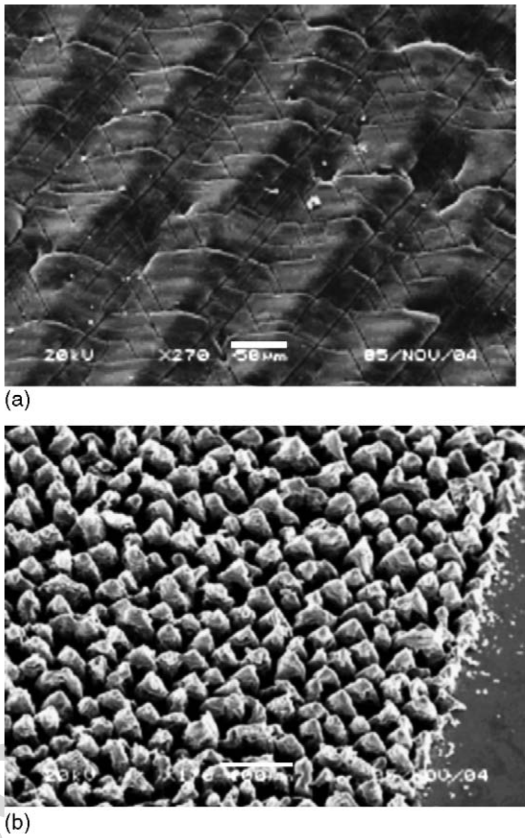


Fig. 1. SEM view of a bare Si surface exposed to 2400 laser shots at 23 J/$cm^2$ (a) and to 3200 shots at 32 J/$cm^2$ (b).

laser fluence. This is the consequence of different wavelength compared to the bandgap laser radiation used in previous works [1–9]. At higher laser fluence the typical array of Si micro-cones is formed as presented in Fig. 1(b). Average spacing between the adjacent micro-cones is 60-70 μm, and they protrude above the initial surface for 10 μm. Same MCA period is also observed on the Au covered Si wafer.

The idea of generation of 3D micro-cones on Au-covered Si is the duplication of conditions of whiskers growth on Si in Si vapors. This growth is known to proceed via so-called vapor–liquid–solid mechanism (VLS) [16]. This mechanism consists in dissolution of Si vapors from a CVD chamber in the liquid eutectic Si–Au which is situated onto a solid Si substrate. Diffusion of Si through this liquid eutectic to the solid substrate results in growth of a Si whisker on the substrate. The layer of Si–Au eutectic remains in a liquid state on top of this whisker providing thus further diffusion of Si through it and further whisker growth. Enlarged SEM view of a single micro-cone is shown in Fig. 2. One can see that Au layer still remains on its surface after the formation of this micro-cone as a discontinuous coating. Detailed study of the tip of a single micro-cone using an atomic force microscope shows that it is covered by some regular protrusions. Their height is about 100 nm and spacing of 200–300 nm. This indicates that the Si transport through a gaseous phase is negligible in our experimental conditions, either with Au film or without it. Therefore, the VLC mechanism does not contribute to the formation of MCA

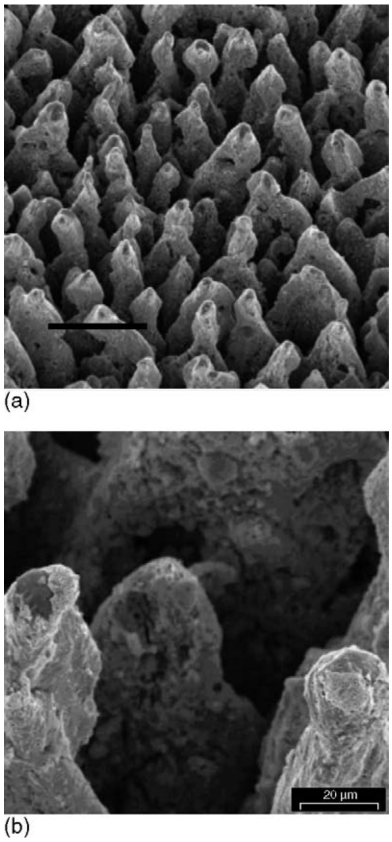


Fig. 2. SEM view of Si micro-cones grown on a Si covered by a 30-nm film of Au. General view, space bar denotes 100 μm (a), enlarged view of micro-cones (b). The sample was treated in an aqueous HF solution after laser exposure.

on Si apparently due to negligible concentration of Si vapours above the sample surface.

The different morphology of MCA grown with a Nd:YAG, such as higher spatial period and higher threshold fluence needed to their formation is due to the different optical properties of Si at the laser wavelength close to the bandgap of this material. Indeed, the absorption of a 1-μm laser radiation in Si is due to a non-linear process of generation of free carriers in its conduction band. The initial absorption is due to various surface defects and contaminations in the sample surface. This absorption is rather weak in a single crystal Si wafer used in the present study, so the MCA formation starts at fluence as high as 20 J/cm$^2$ compared to few J/cm$^2$ of laser radiation in the visible range [7–9]. As soon as the Si surface is damaged by the first laser pulses its absorption increases, and the crystal is molten for a certain depth. This depth should be much higher than the absorption depth of Si at shorter wavelength. Higher thickness of the melt together with relatively long laser pulse of 130 ns results in higher period of capillary waves. These waves are believed to serve as initial inhomogeneity of the relief [7–9].

MCA grown on Si by exposure to radiation of a Nd:YAG laser show the ability towards cold emission of electrons. The *I–V* characteristics obtained with a flat-ended tungsten tip are presented in Fig. 3. The emission current amounts to 40 mA/cm$^2$ (at applied field of 40 V/μm) and is stable at least during testing of the samples. The turn-on field of emission measured with a flat

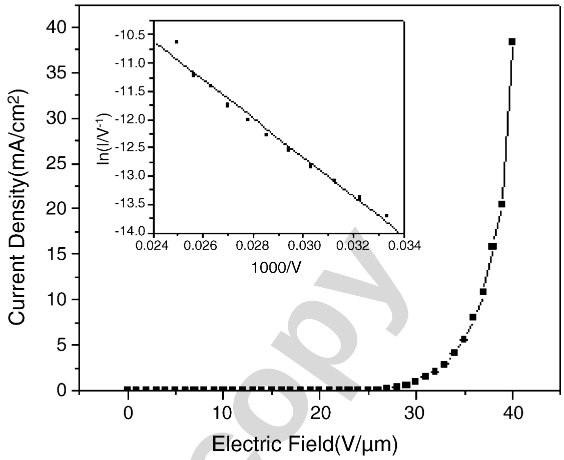


Fig. 3. *I–V* characteristics of electron field emission of MCA on bare Si obtained with a tungsten tip. The inset shows the Fowler–Nordheim fit to the current of field emission.

tip is not sensitive to presence of Au film on initial Si wafer. In both cases the *I–V* characteristics of Si MCA follow the Nordheim–Fowler relation (see inset in Fig. 3). On the contrary, we observe the correlation between the turn-on field of electron emission and processing of the laser-treated samples in an HF aqueous solution. Namely, the samples treated in HF show 20–30% lower turn-on field of emission than the non-treated ones. This observation is coherent with the previously reported [12–14] for micro-cones array on Si generated by a Cu vapor laser. Still, the turn-on fields of emission noticeably decreases if an Au-covered micro-cones were processed in HF after laser treatment. This confirms previous observations on field emission of Si MCA in which their enhanced field emission was attributed to presence of narrow conducting channels in the native oxide layer formed after processing in HF.

Detailed measurements at low emission current indicate that the turn-on field of electron emission is even lower as shown in Fig. 4. It is presumably due to the lower value of emission

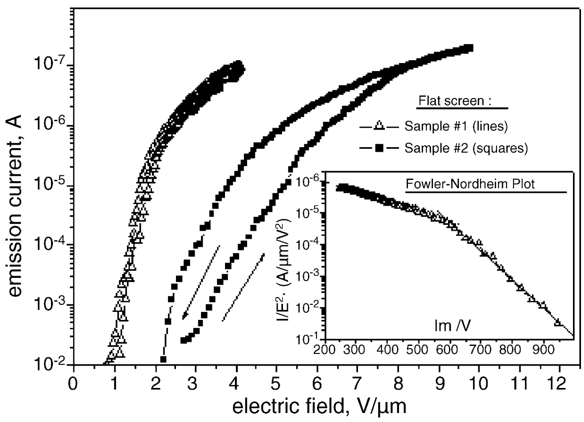


Fig. 4. *I–V* characteristics of the field emission from Si 3D structures grown on an Au-covered Si wafer under its ablation by radiation of a Nd:YAG laser in low vacuum conditions. Flat screen technique, the reference points refer to narrow lines scanned by a laser beam (''lines'') and extended arrays (of 1 mm × 1 mm, ''squares''). Inset shows the Fowler–Nordheim plot to the emission *I–V* characteristics.

threshold for few emitting centers that start to emit at much lower field. In general, the homogeneity of emission from Au-covered Si micro-cones is similar to that measured for a bare Si micro-cones and is lower than that for Si-micro-cones with incorporated carbon nanotubes [14]. Measurements field emission of MCA produced on a bare Si surface at low emission current virtually show the turn-on field of few V/mm as previously reported for MCA grown on bare Si with a Cu vapor laser radiation [12,13].

Fig. 2 shows that Au film on the surface of MCA is not continuous. This should be ascribed to significant increase of the sample surface after the formation of micro-cones array compared to initial flat Si surface. Estimations show [10,11] that this increase is about the factor of 25 without taking into account sub-μm features on the side surface of micro-cones. So a thin (30 nm) Au film cannot remain continuous and is broken into somewhat discontinuous coating. Probably, this is the reason for the observed spatial inhomogeneity of the field emission from Au-covered micro-cones traced with a flat screen technique. This suggestion is partially supported by the fact that narrow lines of micro-cones having the width comparable to the laser spot size show lower turn-on field of emission (see Fig. 4), while extended arrays of micro-cones show higher field. Indeed, the total area of micro-cones in a narrow MCA is lower, and Au film is more homogeneous in this case than in the extended array. One may conclude that the optimal thickness of an Au film should be several times more to guarantee the homogeneity of the cold emission of electrons though in this case it might alter the absorption coefficient of the sample at the laser wavelength. The presence of Au on Si micro-tips may alter the local value of the work function of the material and decrease thereby the turn-on field of electron emission.

Thus, the formation of three-dimensional periodic micro-structures on Si under heating with a pulsed 1-μm laser radiation has been demonstrated. Though Si is transparent at this wavelength, the grown structures have the morphology similar to that obtained by ablation of Si with a bandgap laser radiation (0.51, 0.81, or 0.248 μm). The threshold fluence needed for MCA formation by a 130 ns laser pulses is about 20 J/cm$^2$. The grown MCA demonstrate the field emission of electrons with low turn-on field of few V/μm and overall current density of 40 mA/cm$^2$ at higher fields. The presence of a thin (30 nm) Au film on Si substrate affects both the morphology of the structures and their field emission properties. The turn-on field of electron cold emission is sensitive to the post-treatment of laser-processed Si samples in an aqueous solution of HF.

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