*NANOSTRUCTURES*

# CW laser-induced formation of a nanoparticle ensemble with a bimodal size distribution on PbTe films

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***Abstract***. **We report for the first time the formation of a nanoparticle ensemble on a binary semiconductor (PbTe) film under cw laser irradiation. It is shown that defect – deformation theory of the formation of nanoparticle ensembles in the solid state under cw laser irradiation adequately describes experimental data. In particular, it predicts a bimodal nanoparticle size distribution function that agrees well with the experimental distribution function.**

## 1. Introduction

Laser exposure of semiconductor and metal surfaces is a promising technique for producing nanoparticle ensembles with tailored geometric characteristics (characteristic size and size distribution of the nanoparticles). To this end, a metallic or semiconductor target is typically ablated by high-power femto- (Si) [1], pico- (Ta) [2] or nanosecond (CdTe) [3] laser pulses. Elemental materials are laser-exposed through a liquid layer. The resulting nanoparticle ensembles may have a bimodal size distribution [2, 4].

In this paper, we report for the first time the formation of a nanoparticle ensemble with a bimodal size distribution on semiconductor (PbTe) films exposed to cw laser radiation in air. It is shown that the defect – deformation (DD) theory of the formation of bimodal nanoparticle ensembles [5] adequately describes experimental data for cw laser exposed solid materials, in particular for PbTe targets.

## 2. Experimental

We studied 1.6-μm-thick PbTe semiconductor films grown by molecular-beam epitaxy on (111) Si substrates with a

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thin (2 nm) calcium fluoride buffer layer. The PbTe films were monocrystalline, with their growth direction along [111]. Their surface had a blocky, lamellar structure, with a lateral block size of 1–3 μm and a surface height difference of 10–20 nm (Fig. 1).
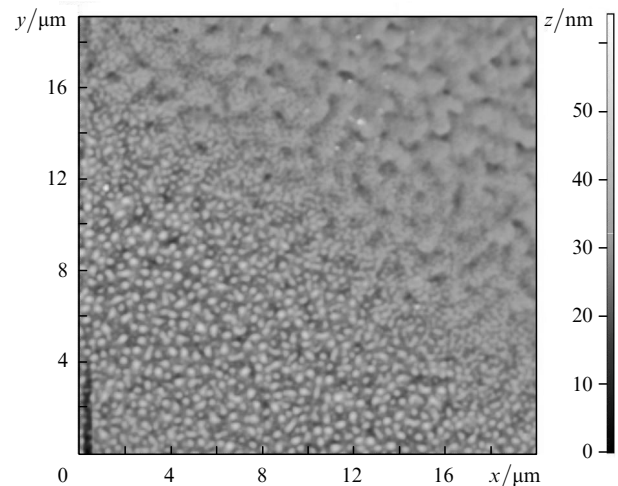


**Figure 1.** Atomic-force microscope image of a PbTe surface after cw laser exposure (8-W power). There is a nanoparticle ensemble formed within the beam spot (bottom left) and a pristine surface (top right). The nanoparticle size decreases with decreasing distance from the interface between the exposed and unexposed regions.

PbTe/CaF$_2$/Si epitaxial structures were exposed to 1.06-μm cw laser radiation (absorption depth $h_{abs} \sim 10^{-5}$ cm [6]) on the lead telluride film side.

The experimental setup was similar to that used in a previous study [7]. A sample was scanned with a laser beam on a positioning stage, which was moved stepwise at 80 μm s$^{-1}$. The irradiation time per point was $\tau_{irr} \sim 3 \times 10^{-1}$ s. The incident laser power was varied from 5 to 10 W. Higher powers resulted in surface melting. At incident powers under 5 W, no changes in surface profile were detected (at a beam spot diameter of 30 μm, 10 W of incident power corresponds to an intensity of $10^5$ W cm$^{-2}$). Surface morphology was examined on a Ntegra Aura atomic force microscope (AFM).

Laser exposure produced a nanoparticle ensemble in the irradiated zone (Fig. 1), with a bimodal lateral size ($\Lambda$) distribution (Fig. 2), which had prominent maxima at $\lambda = 100$ and 300 nm. The distribution function was obtained using the image analysis software supplied with

$n_{dot}$ (arb. units)



**Figure 2.** Experimentally determined normalised lateral size distribution of the nanoparticles.



**Figure 4.** (a) Portion of an irradiated surface with a nanoparticle ensemble and (b) its Fourier spectrum. The strongest maxima are concentrated near three diameters (solid lines) of a circle which are 60° apart (quasi-hexagonal symmetry).

the Ntegra Aura. At an incident laser power of 8 W, the number density of nanoparticles (nanodots), $n_{dot}$, was $5.25 \times 10^8$ cm$^{-2}$. The surface roughness due to the nano-particles ranged in height from 30 to 60 nm. The average lateral size of the nanostructures was found to decrease with increasing distance from the centre of the laser spot (Fig. 3). The spatial distribution of the nanoparticles has a hidden quasi-hexagonal symmetry, which can be revealed by Four-ier transforming an AFM image of the surface (Fig. 4).
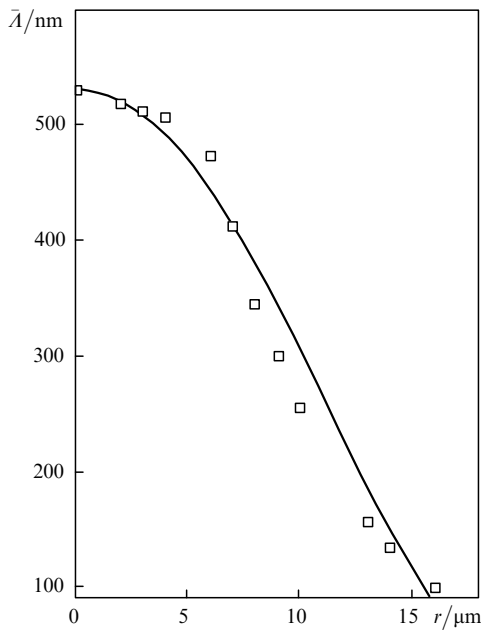


**Figure 3.** Experimentally determined average nanoparticle size, $\bar{\Lambda}$, as a function of distance from the centre of the laser spot, $r$ (open squares). The solid line represents the DD theory prediction [5] for $a = 1.5$ and $r_0 = 18$ μm (see text).

## 3. Discussion

Analysis of Fig. 1 indicates that the film surface was modified through a solid-state process: the original surface morphology can be discerned under the nanoparticles and there is no height difference across the interface between the laser-exposed and unexposed zones. This allows us to interpret the present experimental data in terms of the DD theory of the formation of bimodal nanoparticle ensembles
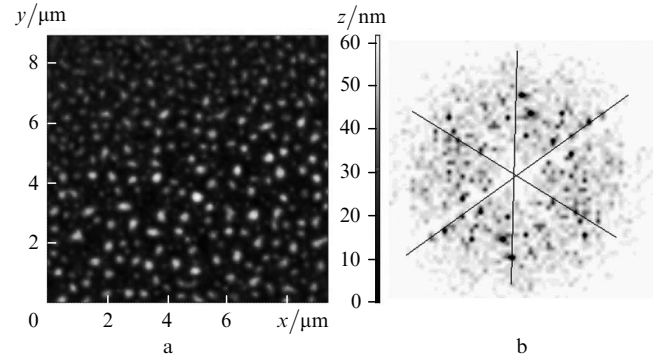
with application to cw laser irradiation in the solid state [5]. The key points of this interpretation are as follows.

The absorption of incident laser radiation over the absorption length, $l_{abs}$, of the semiconductor produces a plasma-enriched surface layer, whose thickness is equal to the carrier diffusion length, $l_{dif} = (D_e \tau_e)^{1/2}$, where $D_e$ and $\tau_e$ are the carrier diffusion coefficient and lifetime, respectively. Recombination-stimulated surface generation of point defects and their diffusion to the bulk lead to the formation of a defect-enriched surface layer of thickness $l_d = (D_d \tau_{irr})^{1/2} < l_{dif}, l_{abs}$, where $D_d$ is the defect diffusion coefficient. At $D_d \sim 6 \times 10^{-11}$ cm$^2$ s$^{-1}$, we have $l_d \sim 5 \times 10^{-6}$ cm.

Under highly nonequilibrium conditions produced by laser irradiation (elevated temperature, mechanical stress, recombination-stimulated diffusion), surface point defects have high mobility. When the defect density exceeds a critical level, the surface layer becomes unstable, and the planar surface geometry gives way to a periodically bent configuration, with accumulations of interstitials and vacan-cies in hillocks and valleys, respectively (DD surface instability [5]). On the sample surface, this is accompanied by an increase in the amplitude of the DD structure, formed by a combination of DD gratings: normal surface displace-ment gratings, $\zeta(\mathbf{r}, t) = \sum_q \zeta_q \exp(i\mathbf{qr} + \lambda_q t)$, coupled with surface defect concentration gratings, $N_d(\mathbf{r}, t) = \sum_q n_d(\mathbf{q}) \times \exp(i\mathbf{qr} + \lambda_q t)$ (where $\lambda_q$ is the growth rate of the DD grating, and $\mathbf{q}$ is parallel to the surface). In the DD theory, a scale parameter which determines a characteristic DD grating period and, hence (according to the DD theory) [5], the nanoparticle size is the thickness of the defect-rich surface layer produced by laser irradiation, $h = l_d$. The reason for the observed decrease in characteristic nano-particle size with increasing distance from the centre of the laser spot (Figs 1, 3) is that the defect diffusion coefficient $D_d$ is temperature-dependent and, for a Gaussian temper-ature distribution in the laser spot, the defect diffusion depth decreases with increasing distance from the centre of the laser spot. Therefore, the scale parameter can be written in the form $h(r) = l_d(r) = l_d(0) \exp\{-a \times [\exp(r^2/r_0) - 1]\}$, where $l_d(0) = [D_d(r = 0)\tau_{irr}]^{1/2}$ is the defect diffusion depth in the centre of the laser spot; $r_0$ is the spot radius; $a = E_d^*/(2k_B T(r = 0))$; $E_d^*$ is a reduced activation energy for recombination-stimulated defect diffusion; and $T(r = 0)$ is the temperature in the centre of the laser spot.

Since the nanoparticle size at a distance $r$ from the centre

of the laser spot is proportional to $h(r)$ [5], the average nanoparticle size $\bar{\Lambda}$ (in microns) in a nanoparticle ensemble is also proportional to $h(r)$: $\bar{\Lambda}(r) = 530 \exp\{-a \times [\exp(r^2/r_0^2) - 1]\}$. At $r_0 = 18$ μm and $a = 1.5$, the DD theory adequately describes the variation of the experimentally determined average nanoparticle size $\bar{\Lambda}$ with distance from the centre of the spot (Fig. 3).

According to Emel'yanov [5], at sufficiently high defect densities the growth rate of a DD grating, $\lambda_q = \lambda_q(\Lambda)$ is a bimodal function of its period, $\Lambda = 2\pi/q$. Because of the (111) crystalline anisotropy of the substrate (or nonlinear three-wave interaction of the DD gratings on an isotropic surface [5]), DD instability development on the semiconductor surface leads to the formation of a hexagonal cellular seed DD superstructure in which the particle size distribution of $\Lambda$ cells (nanoparticle nuclei) is governed by the bimodal growth rate $\lambda_q = \lambda_q(\Lambda)$ [5]. The formation of such a hexagonal surface structure under the experimental conditions of this study is demonstrated by Fourier transforms of micrographs of the irradiated surface (Fig. 4).

The spatially periodic defect distribution in a seed DD structure leads to a spatially periodic modulation of the vaporisation rate of atoms on the semiconductor surface being irradiated: the vaporisation rate is higher in the valleys, which contain accumulations of vacancies, in comparison with the hillocks, which contain accumulations of interstitials. As a result, the sample surface irreversibly acquires a hexagonal cellular structure (of nanoparticles). The nanoparticle size distribution function then replicates the cell size distribution function in the seed DD structure, which can be expressed through the bimodal growth rate $\lambda_q = \lambda_q(\Lambda)$ [5].

Figure 5 compares the calculated nanoparticle size distribution function [5] to the present experimental data (Fig. 2).

The calculated nanoparticle size distribution (Fig. 5) has maxima at $\Lambda_c = 10^{-5}$ cm (S peak) and $\Lambda_m \approx 3 \times 10^{-5}$ cm (L peak), in agreement with the experimental data in Fig. 2. The curve adequately represents the experimentally determined distribution over the whole range of nanoparticle sizes detected. Thus, the DD theory [5] adequately describes the entire set of experimental data obtained in this study.

In conclusion, note that the observed cw laser-induced formation of nanoparticles on the binary semiconductor PbTe prompts a relatively simple, easy-to-control process for producing nanoparticle ensembles. Additional theoretical and experimental studies are needed to address issues pertaining to the preparation and practical application of narrowly sized nanoparticle ensembles in this approach.

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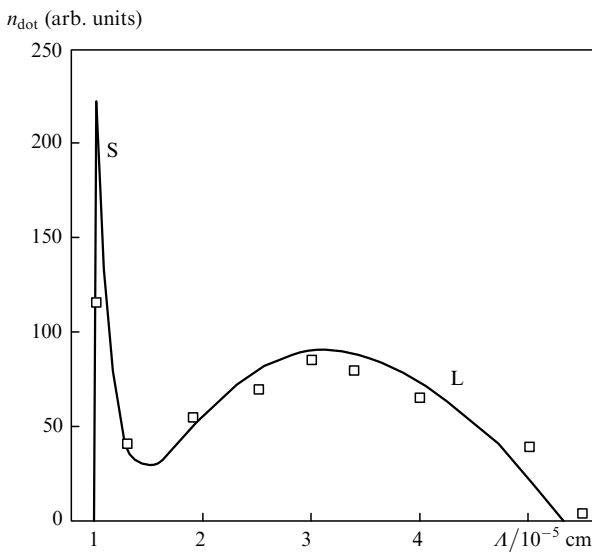
**Figure 5.** Calculated normalised bimodal lateral size distribution of nanoparticles (solid line) {formula (11) in Ref. [5], where $\varepsilon = 57$ and $C = 5$; the other parameters are specified in text [5]}. The open squares represent the experimental data in Fig. 2. The coefficient $C$ is a normalisation factor which was determined by fitting to the experimental data.