Laser induced effects on ZnO targets upon ablation at 266 and 308 nm wavelengths

María Jadraque,^{1,a)} Concepción Domingo,^{2,b)} and Margarita Martín^{1,c)}

¹*Instituto de Química Física "Rocasolano," C.S.I.C. Serrano 119, 28006 Madrid, Spain*

²*Instituto de Estructura de la Materia, C.S.I.C. Serrano 121, 28006 Madrid, Spain*

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The development of structural changes in ZnO targets, upon laser irradiation at the wavelengths of 266 and 308 nm, is studied by Raman spectroscopy. At the wavelength of 308 nm, oxygen vacancies are found to develop monotonically with increasing laser intensity. At 266 nm, a structural change in the irradiated ZnO targets, possibly related to nanostructuring, is observed above the laser fluence of 0.45 J cm^{-2} . The different natures of the laser target interaction processes taking place at both wavelengths are investigated through the characterization of the composition and energy distribution of the species ejected in the ablation. The energy of the neutral Zn and Zn_2 present in the ablation at 308 nm shows a smooth dependence on laser fluence which is consistent with the observed smooth development of oxygen vacancies. At 266 nm, the average kinetic energy of the ejected fragments is higher than at 308 nm and changes abruptly with the ablating laser fluence, consistently with the presence of a fluence threshold above which structural transform is observed at this wavelength. The plume shows the same neutral composition (Zn, ZnO, and Zn_2) at both wavelengths but the dependence on fluence of the ratio of neutral atomic Zn to the dimer Zn_2 shows significant differences. From the latter, different temperature regimes can be inferred in the plume generated at both wavelengths. At 266 nm the cationic composition of the plume is mainly stoichiometric whereas at 308 nm $\text{ZnO}_{2(3)}\text{H}_{2(1)}^+$ cations have the highest intensity. © 2008 American Institute of Physics. [DOI: 10.1063/1.2956707]

I. INTRODUCTION

Pulsed laser deposition (PLD), from ZnO targets, is known to be an efficient way to generate ZnO films and nanostructures of different quality and properties.^{1–5} Laser induced modifications of the target surface during PLD have been invoked as possible reasons for the appearance of defects in the final deposits. At the ablation wavelength of 193 nm (Ref. 1) and at high laser fluences, near 20 J cm^{-2} , Zn enrichment of the postablated surface has been reported and attributed to redeposition of Zn on the target by condensation of the less volatile component of the dense plume produced at high laser fluence. This laser induced Zn enrichment of the target after several laser shots during the PLD process has been assumed to lead to formation of nonstoichiometric films with a ratio Zn:O greater than unity. Also, to explain the ejection of double charged Zn^{2+} below the ablation threshold at 248 nm, it has been suggested that it comes from regions with a high density of laser induced defects.⁶ The presence of lattice defects, as oxygen vacancies⁷ has been found to influence the photoluminescence properties of ZnO nanostructures obtained by PLD. On the other hand, target surface modifications can lead to a

different composition of the ablation plume; for instance, it has been reported that ablation of etched surfaces of ZnO targets, leads to a higher proportion of stoichiometric free clusters in the plume, than those obtained from fresh surfaces.⁸

A better control of the above deposition process could be achieved through the knowledge of the way in which target modifications develop as the laser ablation proceeds and influence the composition of the ejected material. In this work, aiming at getting some insight on the laser interaction processes involved in the development of defects on ZnO targets and its potential influence on the final deposits in PLD, we have investigated the relationships between the nature of the target modifications and the plume characteristics upon ablation at 308 and 266 nm wavelengths. Preliminary work carried out in our laboratory has reported the development of laser induced defects in ZnO targets at the above wavelengths;⁹ in the present work we have characterized in detail their dependence on laser fluence.

II. EXPERIMENTAL

Pellet targets of pressed ZnO powder (purity > 99.1%) were ablated in a multiple shots mode by a XeCl excimer laser and by the fourth harmonic output of a Nd:yttrium aluminum garnet laser (wavelengths of 308 and 266 nm, respectively) under vacuum conditions better than 2×10^{-6} mbar. The ablating laser beams were limited by several apertures and focused by a quartz lens (focal length of 50 cm), forming the focal point at distances ≥ 0.7 cm from the target sur-

^{a)}Author to whom correspondence should be addressed. Electronic mail: jadraque@iesl.forth.gr. Present address: Institute of Electronic Structure and Laser, FORTH. P.O. Box 1527, Heraklion, GR-71110, Crete, Greece. Tel.: +30 2810 391325.

^{b)}Electronic mail: cdomingo@iem.cfmac.csic.es. Tel.: +30 91 5616800, FAX: +30 915645557.

^{c)}Electronic mail: mmm@iqfr.csic.es. Tel.: +30 91 5619400, FAX: +30 91 5642431.

FIG. 1. Raman spectra of ZnO targets irradiated at 266 nm with laser fluence F (a) $F < 0.25 \text{ J cm}^{-2}$ (b) $F > 0.45 \text{ J cm}^{-2}$.

face. The unfocused beam profiles can be described by a top hat at 308 nm and by a Gaussian intensity distribution at 266 nm.

Raman spectra of irradiated targets were acquired in a Renishaw RM2000 confocal Raman microscope, using as excitation the 514.5 nm line provided by an air-cooled Ar⁺ laser. Laser power was 1.5 mW at the laser exit. The scattered radiation from the surface was collected in backscattering (180°) geometry at a resolution of 4 cm^{-1} . The size and depth of the laser craters on the target were measured with the $50\times$ objective of the Raman microscope employed for taking also the spectra.

Time-of-flight mass spectroscopy was used to study the composition and dynamics of the ablation plume. The experimental setup has been described in previous works.^{10,11} Briefly, laser ablation and expansion of the plume took place in the extraction region of a linear time-of-flight mass spectrometer. The positive ions were deflected along the flight axis by a pulsed electric field ($70\text{--}160 \text{ V cm}^{-1}$) and accelerated under a total voltage of 2000 V. Ions were detected by a dual set of microchannel plates. The neutral species in the plume were postionized by an ArF laser (at 193 nm) that interacted with the plume perpendicularly to the ablating laser and to the flight axis of the spectrometer. The postioniz-

ing laser pulse probed the plume at different delay times with respect to the ablating laser and at different distances from the target surface.

III. RESULTS AND DISCUSSION

A. Raman analysis of the laser induced changes in the ZnO targets at the wavelengths of 266 and 308 nm

The Raman spectra of targets irradiated at 266 nm are shown in Fig. 1. At fluences below 0.25 J cm^{-2} the spectrum reveals the wurtzite structure¹² having C_{6v}^4 or 6 mm symmetry. The observed bands centered at 380 (TO), 407 (TO), 435, and 576 (LO) cm^{-1} , shown in Fig. 1(a), correspond to A_1 (transverse), E_1 (transverse), E_2 , and A_1 (longitudinal) symmetries of the fundamental optical modes, respectively. Furthermore, Raman bands corresponding to multiphonon processes are also observed around 329, 610, 980, and 1148 cm^{-1} . This spectrum is similar to the nonirradiated ZnO.¹² At fluences above 0.45 J cm^{-2} , the E_2 mode is blue-shifted and surpassing broadened [Fig. 1(b)]. The band centers and the full width half maximum (FWHM) obtained by Lorentz fitting are listed in Table I. Note that the FWHM of the 435 cm^{-1} band is doubled at 0.45 J cm^{-2} .

The width, position, and intensity of the TO phonon mode band at 435 cm^{-1} are known to be very sensitive to structural changes such as disorder, residual stress, and thermal heating or phonon confinement effects, possibly related to nanostructuring. In most of the Raman spectra of nanoparticles, the first-order Raman peak redshifts and broadens toward the low-wave-number side, as the nanoparticle size decrease;^{13,14} however, unexpected upward shifts have also been observed in nanoparticles embedded in a glass matrix.¹⁴ The above suggests that the structural changes observed in the Raman spectra might be due to the formation of nanostructured centers in the targets, above certain laser fluence.

In ZnO layers produced by PLD, laser annealing, at the laser wavelength of 193 nm and fluences $\geq 0.14 \text{ J cm}^{-2}$ leads to coalescence of ZnO nanoclusters.¹⁵ This has been explained by the melting of the ZnO surface at these fluences. In the same PLD process, photoluminescence observed in the trajectory of the 193 nm laser beam, in a narrow range of laser fluences, is attributed to condensation of ZnO free nanoclusters.⁸ In the experiments reported here, the higher

TABLE I. Frequencies and FWHM of nonirradiated ZnO targets and irradiated at 266 nm ($F < 0.25 \text{ J cm}^{-2}$ and $F > 0.45 \text{ J cm}^{-2}$).

Nonirradiated ZnO target		ZnO targets irradiated at 266 nm at $F < 0.25 \text{ J cm}^{-2}$		ZnO targets irradiated at 266 nm at $F > 0.45 \text{ J cm}^{-2}$	
Frequency (cm^{-1})	FWHM	Frequency (cm^{-1})	FWHM	Frequency (cm^{-1})	FWHM
380 ^a	16	380	16	380	58
435 ^b	11	435	11	437	22
576 ^c	30	576	31	576	37

^a A_1 (transverse),

^b E_2 .

^c A_1 (longitudinal).

FIG. 2. Mapping picture of the crater produced in the ZnO target upon laser irradiation at 308 nm. Near the centre of the crater laser fluence is $\sim 0.8 \text{ J cm}^{-2}$. Raman spectra recorded scanning the crater from the outer part (upper part) toward its center (lowest part).

excess energy of the 266 nm photon (with respect to the band gap) is carried as electron kinetic energy and transferred to the lattice. We suggest that above a given fluence, surface temperature reaches values that can cause “annealing” of the target giving rise to the observed structural changes.

Upon laser irradiation at 308 nm the Raman spectra recorded scanning the craters at different distances from their center show a gradual change as depicted in Fig. 2. At the outer part of the crater, the Raman spectrum, shown in the upper part of Fig. 2, corresponds to the characteristic spectrum of the wurtzite structure similarly as observed in non-irradiated areas. Scanning the crater toward its central region, several differences gradually arise in the Raman spectrum: the band at 576 cm^{-1} shift to 556 cm^{-1} , the mode E_2 at 436 cm^{-1} disappears and two bands appear at 170 and 223 cm^{-1} . Near the center of the crater, the Raman spectrum, shown in the lowest part of Fig. 2, is similar to that recorded from polycrystalline ZnO thin films; in these, the bands are attributed to oxygen vacancies.¹⁶ A slopping background is also observed in these Raman spectra that can be attributed to visible luminescence produced in the postablated areas.¹⁴

The above results show that oxygen vacancies are developed on the ZnO target surface by 308 nm laser irradiation. Moreover, the monotonic development of the characteristic Raman spectra indicates that the oxygen vacancy concentration increases monotonically toward the crater center in the same way that the laser fluence distribution on the crater; the latter corresponds to the nearly Gaussian profile of the energy distribution across the transversal section of the focused laser beam.

Previous works have reported that irradiation by laser light at 308 nm produces color changes in several metal oxides that have been attributed to oxygen vacancies in the surface regions;¹⁷ for ZnO it was reported that a nearly negligible effect could be observed at low fluences and strong ablation at the fluences above 1 J cm^{-2} , but no further characterization was carried out in this material. The Raman analysis reported in the present work, clearly demonstrates the formation of oxygen vacancies probably associated with the laser generation of electron-hole pairs. The energy of the

FIG. 3. Zn and Zn_2 signal intensity (obtained by integrating the Zn and Zn_2 mass peaks of the time-of-flight mass spectrum of the postionized plume) vs the delay between the pulses of ablation and postionization. Full squares $\blacksquare$ correspond to the Zn signal; open circles $\circ$ correspond to Zn_2 . (a) The ablation wavelength is 308 nm. (b) The ablation wavelength is 266 nm.

308 nm photons (4.04 eV) is higher than the enthalpy of neutral oxygen formation in ZnO (3 eV) but smaller than the energy needed to form a Zn vacancy (5.41 eV).¹⁸

In order to understand the differences in the laser/target interactions that influence the different structural changes observed at either wavelength, in the next section we have further characterized the process, obtaining information on the energy exchanged in the ablation.

B. Energy of species produced in the ablation at 266 and 308 nm.

Figures 3(a) and 3(b) show the time distributions of the neutral Zn and Zn_2 , observed in the ablation plume at 308 and 266 nm. The time distributions were obtained recording the mass spectra of the postionized plume at different delays between the pulses of ablation and postionization. The intensity of the Zn and Zn_2 mass peaks obtained at each delay was plotted versus time delay. The mass spectrum of the plume is depicted in Fig. 4.

At 266 nm time distributions of Zn and Zn_2 were measured at the fluences of 0.25 and 0.45 J cm^{-2} , respectively, below and at the value at which structural changes are observed. At 308 nm the fluences were in the range of 0.15 – 1.15 J cm^{-2} .

The time distributions $I(t)$ can be converted to kinetic energy distributions $f(E)$ by using the transformation expression: $f(E) \propto I(t)t^3$ that applies under the present experimental conditions in which the signal intensity I , is proportional to the integrated density of neutral species in the column of the

FIG. 4. Mass spectra of the ablation plume of ZnO targets. (a) Neutral species observed at the laser wavelengths of 266 and 308 nm. (b) Positive ions observed at the laser wavelength of 266 nm. (c) Positive ions at the wavelength of 308 nm.

plume probed by the postionizing laser.¹⁹ The average kinetic energy $\langle E_{\text{kin}} \rangle$ can be obtained from $f(E)$ as $\langle E_{\text{kin}} \rangle = \int f(E) E dE / \int f(E) dE$. The values obtained are listed in Table II.

The kinetic energy values are too high to be conciliated with ablation mechanisms of thermal origin, which is not unexpected as the photon energy at both ablation wavelengths is larger than the direct energy gap of the material (3.35 eV). A detailed discussion on the possible ablation mechanisms is out of the scope of this work; however, we would like to focus attention on the significant differences in the dependence of the average kinetic energies on laser fluence shown at 266 and 308 nm.

At 308 nm $\langle E_{\text{kin}} \rangle$ increases weakly with fluence, whereas at 266 nm a pronounced dependence on laser fluence is obtained. Thus, at 308 nm, the weak dependence on fluence of the $\langle E_{\text{kin}} \rangle$ is consistent with the smooth (gradual) development of oxygen vacancies when the ablation crater is scanned from its outer region towards its center. On the contrary, at 266 nm, the $\langle E_{\text{kin}} \rangle$ at the fluence of 0.45 J cm^{-2} , for which structural changes in the target become detectable, is twice the value obtained at 0.25 J cm^{-2} , where no target modification can be observed.

The other significant difference is the signal intensity of the dimer Zn₂ relative to Zn. As depicted in Fig. 3, at 308 nm, the ratio between the respective time-integrated intensities of Zn₂ and Zn remains roughly the same in the

TABLE II. Ablation of ZnO targets at 266 and 308 nm. Average kinetic energies of Zn and Zn₂ in the plume, derived from the experimental time distributions at two different laser fluences.

	266 nm		308 nm	
	$F/\text{J cm}^{-2}$	$\langle E_{\text{kin}} \rangle/\text{eV}$	$F/\text{J cm}^{-2}$	$\langle E_{\text{kin}} \rangle/\text{eV}$
Zn	0.25	1.4	0.15	1.2
	0.45	2.7	1.15	1.5
Zn ₂	0.25	1.1	0.15	1.3
	0.45	2.7	1.15	1.4

range of fluences from 0.15 to 1.15 J cm^{-2} , whereas at 266 nm this ratio is five times smaller at the higher fluence. A suitable explanation is that the plume temperature rises to the value at which the average vibrational energy of the dimer becomes comparable to its dissociation energy. Experimental and computational data²⁰ set the dissociation energy of Zn₂ in 0.03 eV, therefore temperatures about 800 K would account for the lower dimer signal. From this data it can be estimated that temperatures higher than 800 K are reached in the plume ejected from the heated target, upon ablation at 266 nm and 0.45 J cm^{-2} .

C. Plume composition from postablated targets

Finally, we have investigated whether the stoichiometry of free clusters present in the ablation plume could be related to the structural changes observed in the postablated ZnO targets. As shown in Fig. 4(a), Zn, Zn₂, and a weak contribution from ZnO were the only neutral species observed in the plume at both laser wavelengths. The positively charged species, at the laser fluences at which structural changes develop in the target, are shown in Figs. 4(b) and 4(c). At 266 nm the mass peaks obtained can be assigned to ZnO⁺ and Zn₂O₂⁺. At 308 nm the features at 98, (113), 162, and (178) amu are tentatively assigned to ZnO₂H₂⁺, ZnO₃H⁺, Zn₂O₂⁺, and Zn₂O₃⁺. This assignment to mono- and dihydrogenated clusters was confirmed by testing their stability by density functional theory calculations. The calculated geometries were optimized at the same level and energy minima structures were confirmed by frequency calculations.

The calculations gave stable structures for the hydrogenated clusters and nonbonding geometries for the corresponding bare ZnO₂⁺ and ZnO₃⁺. The optimized structures of ZnO₂H₂⁺ contain a linear O–Zn–O group with one of its O atoms bound to the two H. ZnO₃H⁺ is a peroxostructure (O–O–Zn–O–H). A better description of the computational results will be presented and discussed elsewhere. Formation of mono- and dihydrogenated clusters have also been reported in the ablation of ZnO (Refs. 21 and 22) and of ZnS targets and similarly as reported here, only for low masses where the corresponding nonhydrogenated clusters were not observed in the mass spectra.²³

The stabilization of ZnO surfaces by OH groups has been associated with the formation of oxygen vacancies and other defects.²⁴ The presence of SiOH defects in porous siliceous targets has been proposed to influence the formation and stability of hydrogenated clusters in the ablation plume of these materials²⁵ in a similar way as the hydrogenated species observed here.

In summary, we can conclude that different plume compositions are obtained from ZnO ablated at fluences higher than those required to observe structural changes: at 266 nm stoichiometric ZnO⁺ predominate whereas at 308 nm ZnO₂H₂⁺ and Zn₂O₂⁺ have the highest signal intensity; these differences are somehow related to the different structural changes induced in the target at both wavelengths.

IV. CONCLUSIONS

The formation of structural changes in ZnO targets upon ablation at the laser wavelengths of 266 and 308 nm has been investigated. Raman analysis of the postablated targets identifies the presence of structural changes (possibly related to nanostructuring) at the laser wavelength of 266 nm above a given threshold, whereas, upon ablation at 308 nm, oxygen vacancies develop smoothly with increasing laser energy.

The composition and dynamics of the plume show significantly different dependences on laser fluence of the ratio between the atom Zn and the dimer Zn₂, at each wavelength. From this, two different temperature regimes can be inferred in the ablation plume obtained at each wavelength; plume temperature can be estimated in values over 800 K upon 266 nm ablation at fluences above 0.45 J cm⁻² whereas a lower temperature regime holds in the whole range of fluences investigated at 308 nm.

We conclude that upon ablation at 266 nm and above a given fluence, annealing of the target takes place due to rise of the temperature at values higher than 800 K; on the other side, laser generation of electron-hole pairs is associated with the formation of oxygen vacancies at 308 nm. In the latter case, the monotonically increasing development of defects upon increasing laser fluence could provide a way to a controlled generation of defects on those targets.

The different stoichiometries of the species in the plume are affected by the surface induced defects, in support of the observations that relate surface modifications and the properties of ZnO nanostructures obtained by PLD.

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