Correlation between plasma dynamics and porosity of Ge films synthesized by pulsed laser deposition

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The porosity of Ge films deposited by pulsed laser deposition in an inert gas atmosphere is observed to be directly correlated with the kinetic energy of ablated species. The deposition conditions were modified by varying the pressure and the target-substrate distance. The evolution of the kinetic energy of ablated species as a function of deposition parameters, such as distance from target and background gas pressure, is described in terms of a theoretical model. The relationship between the density of Ge films and the kinetic energy of ablated species is discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2356689]

Pulsed laser deposition (PLD) is considered a versatile method for the growth of thin films from almost any kind of solid and liquid target materials.[1,2] Focusing a laser beam on a target results in the creation of a plasma, which expands in the direction perpendicular to the target surface, and in the deposition of thin films.[1] This deposition technique offers many advantages and a great flexibility, as for example, the possibility of achieving thin films from multicomponent targets. Variation of the deposition conditions yields significant changes in film properties, such as their density. It has been demonstrated that deposition under vacuum conditions yields dense films, whereas an inert gas environment favors the synthesis of nanoparticles with a controlled size.[3,4] On the other hand, any change of the micro-nanostructure will affect the film properties (i.e., electrical, mechanical, optical characteristics, etc.).[5]

In the study of PLD processes, significant efforts have been devoted to the investigation of plasma expansion dynamics in ambient gases of various compositions by means of temporally and spatially resolved plasma diagnostics.[6,7] The knowledge of the plasma plume characteristics and its dynamic behavior is particularly important in understanding how film growth mechanisms are related to the deposition parameters.

A preliminary study correlating gold film microstructure with plasma expansion parameters was reported by Irissou *et al.*[8] This study demonstrated that variations in the gold deposition kinetic energy (from 130 to 0.01 eV) strongly influence the structure of gold films,[9,10] resulting in nanocrystals at low deposition energies and highly oriented films at high energies.

In this letter, we investigate the influence of the kinetic energy of the ablated germanium species, in flight toward a substrate through an inert gas atmosphere, on the characteristics of Ge films deposited on the substrate. Using time and space resolved plasma emission spectroscopy, we correlate the plasma expansion dynamics (kinetic energy of deposition) to the density of the Ge films. A quantitative demonstration of the flexibility of the PLD technique resulting from the wide range of deposition kinetic energy is thus clearly provided for Ge, a widely used semiconductor.

Germanium films were deposited by conventional PLD in a helium gas atmosphere. The Ge target (purity of 99.999%) was ablated with a focused laser beam (KrF laser, $\lambda=248$ nm, pulse length of 17 ns, and repetition rate of 20 Hz). The laser fluence was set at 9 J/cm^2, while the target-substrate distance was varied from 25 to 60 mm and the He pressure from 0.1 to 10 Torr. The deposited films were analyzed by scanning electron microscopy (SEM) and x-ray reflectivity (XRR).

The expansion of the neutral Ge species ejected from the target was investigated by time-of-flight (TOF) emission spectroscopy, using the experimental setup described in Ref. 9. Plasma "slices" of 0.4 mm^2 surface were imaged perpendicularly to the plasma expansion direction using a pair of planoconvex lenses (focal length of 35 cm) onto the entrance slit (4 mm high and 100 μm wide) of a 50 cm Czerny-Turner spectrometer. The spatially resolved intensity of the most intense neutral Ge *I* line at $\lambda=303.9$ nm (radiative time of 6 ns)[11] is measured along the plasma expansion direction with steps of 5 mm. The signal was recorded using a gated intensified charge-coupled device (Andor). Temporal resolution was achieved by triggering the emission intensity measurement and recording at preset delays with respect to the laser pulse. For a given distance from the target, we measured the time delay at which the maximum emission intensity of the Ge *I* line occurs. This maximum intensity is associated with the plasma front, which is sometimes associated with the Knudsen layer.[12,13]

Figure 1 shows the spatial position of the plasma front as a function of time (time of flight) for various He pressures. For each distance the TOF of the ablated species increases significantly with pressure, which indicates that the kinetic energy is smaller at higher pressures. To describe the motion of the plasma front, various models have been proposed.[8,9] Among these models, the drag model[14] is not suitable for Ge plasmas at intermediate He pressures (between 0.5 and 2 Torr), while the shock-wave model[14] does not describe properly the expansion at high pressure (>1 Torr He). To fit our data, we used the model of colliding hard spheres.[15,16] The experimental data $x(t)$ shown in Fig. 1 were fitted with a logarithmic function $x=\ln(1+kv_0t)/k$ obtained from the model with a coefficient k and an initial velocity of ablated species v_0.[15] The velocity $v=dx/dt$ and the kinetic energy

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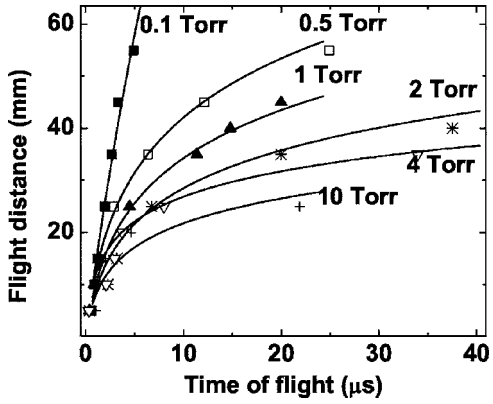

FIG. 1. Flight distance as a function of the time of flight of the plasma front for He atmosphere pressures from 0.1 to 10 Torr.

$E=m_{\mathrm{Ge}}v^2/2$ of the plasma front were determined from the fitted curves. Figures 2(a) and 2(b) display the dependence of the kinetic energy on the target-to-substrate distance [Fig. 2(a)] and on the gas pressure [Fig. 2(b)]. In Fig. 2(b) the straight lines connect the model predictions for the pressure values of Fig. 2(a). The kinetic energy of the plasma is observed to decrease with increasing He pressure. These figures show that the kinetic energy is strongly influenced by both gas pressure and distance. Clearly, while the model accurately describes the dependence of the kinetic energy on the pressure at long distances (25 and 35 mm) from the target, the model fails to describe the experiments for shorter distances (10 mm). At such short distances, the plasma is very dense and the probability of collisions between Ge atoms is therefore high. Since the model does not consider Ge–Ge collisions, its validity for short distances is questionable.[17]

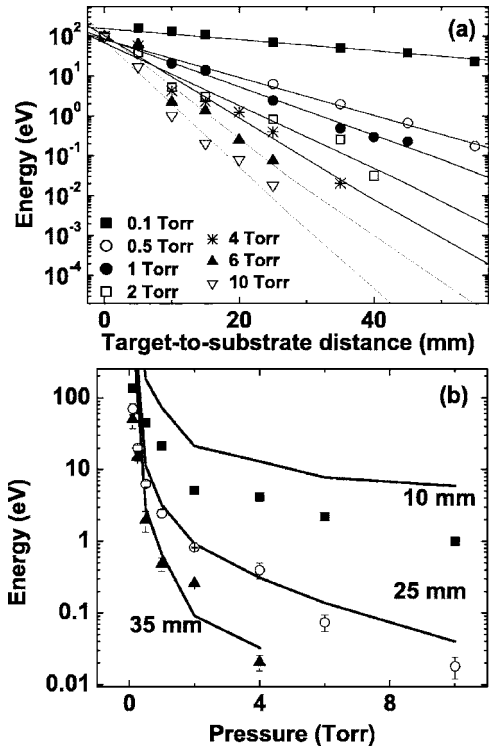

FIG. 2. (a) Kinetic energy of the plasma front as a function of target-substrate distance (ranging from 5 to 60 mm) for different He pressures (from 0.1 to 10 Torr); (b) kinetic energy as a function of background gas pressure for different target-substrate distances.

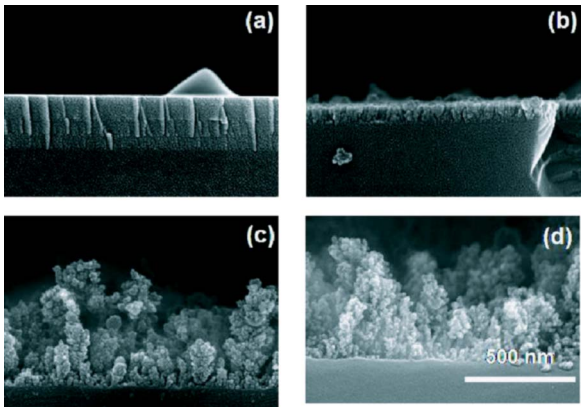

FIG. 3. SEM images of different types of films deposited by laser ablation at room temperature in inert gas atmosphere. Deposition conditions: target-substrate distance of 40 mm, laser fluence of 9 J/cm^2, and background He pressures of (a) 0.1 mTorr, (b) 1 Torr, (c) 4 Torr, and (d) 10 Torr.

The TOF technique allows the determination of the kinetic energy of the ablated species assuming that their velocity is equal to the velocity of the plasma front. We note that in the low energy region (a few tenths of eV), the thermal energy of excited plasma species cannot be neglected in comparison with the streaming energy.

To investigate the relationship between the kinetic energy of ablated species and the microstructure of the deposited films, we have studied the structural properties of the Ge films. Figures 3(a)–3(d) display SEM images of the films deposited under a He pressure varying from 0.1 to 10 Torr, with a target-substrate distance of 40 mm and a laser fluence of 9 J/cm^2. The four micrographs show that at the lowest He pressure of 0.1 Torr, the film is dense, then slightly porous at 1 Torr, noticeably porous with a vertically grown structure at 4 Torr, and finally exhibits an isotropic porous structure at 10 Torr.

A quantitative analysis of the Ge film density for various deposition conditions was performed by XRR (Refs. 18 and 19) from the observed critical angle θ_c.[20] Figure 4 shows the density of the Ge films thus obtained as a function of the kinetic energy of the ablated species. This figure clearly demonstrates that the density increases from

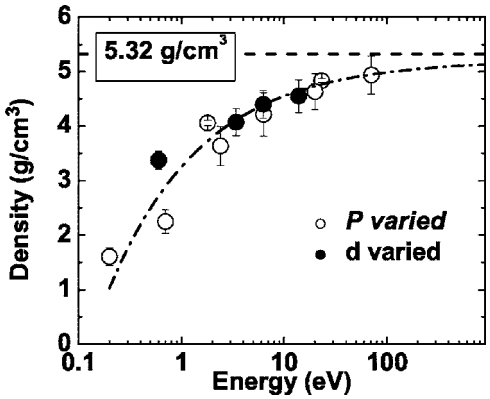

FIG. 4. Ge film density as a function of kinetic energy per atom of ablated species. Because the plasma front kinetic energy can be controlled indirectly via two parameters, i. e., gas pressure P (d=25 and 60 mm) and distance d (P=0.25 Torr), we use the open and solid symbols to show when we varied the pressure and the distance, respectively. At the highest energies the density approaches the horizontal dashed line indicating the Ge bulk density of 5.32 g/cm^3.

0.4 to 4.9 g/cm^3 as the kinetic energy per atom is increased from 0.2 to 70 eV and tends toward the bulk density indicated by the dashed line at 5.32 g/cm^3. With the kinetic energy being controlled via pressure and distance variations, this universal curve shows that the kinetic energy per atom is indeed the relevant direct parameter controlling the film density in a very wide range.

In conclusion, we examined how the density of Ge films deposited by PLD is related to the kinetic energy of the ablated species. A significant variation of the Ge film density (from 4.9 to 0.4 g/cm^3) was observed as the kinetic energy of the species decreases from 70 to 0.2 eV. In PLD, this kinetic energy can be controlled by convenient choice of background pressure and of the substrate-to-target distance. The wide range in variation of the kinetic energy of deposition makes PLD a very suitable technique to use for precision tuning of film structure and properties.

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[16] The hard-sphere model described in Ref. 15 is briefly summarized as follows. Assuming hard-sphere collisions between heavy plume and light gas background, the loss of directed velocity of the heavy plume atoms/ions varies as the square of the velocity. The main approximations of the model are (1) $m_{Ge} \gg m_{He}$, (2) $v_{Ge} \gg v_{He}$, and (3) all the collisions are elastic. m_{Ge} and m_{He} and v_{Ge} and v_{He} are the masses and the velocities of Ge and He atoms, respectively. Despite its rather strong assumptions, this simplified model works quite well. Improvements would require significant kinetic modeling.
[17] In addition, the vertical resolution R_v of the spectrometer in TOF measurements is typically 10 mm. As a consequence, the measured emission signal is due to ablated species located at different flight distances (all the flight distances between x and $\sqrt{x^2+R_v}$). Clearly, the vertical resolution is negligible only for distances significantly larger than R_v.
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[20] Below the critical angle $\theta \leqslant \theta_c$, total reflection occurs, whereas at $\theta \geqslant \theta_c$, x rays are partially absorbed by the sample. The critical angle $\theta_{c,\mathrm{film}}$ can thus be determined from the sharp changes in reflected x-ray intensity. $\theta_{c,\mathrm{film}}$ is related to the film density ρ_{film} using the following expression: $\rho_{\mathrm{film}} = (\theta^2_{c,\mathrm{film}}/\theta^2_{c,\mathrm{bulk}})\rho_{\mathrm{bulk}}$, where ρ_{bulk} and $\theta_{c,\mathrm{bulk}}$ are the density and the critical angle of bulk material, respectively.