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Citation: Appl. Phys. Lett. **101**, 031911 (2012); doi: 10.1063/1.4737654
View online: http://dx.doi.org/10.1063/1.4737654
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v101/i3
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Plasmonic mediated nucleation of resonant nano-cavities

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(Received 15 June 2012; accepted 3 July 2012; published online 19 July 2012)

We show that the energy required for nucleation can be efficiently supplied by the electromagnetic field in resonance with plasmonic oscillations of a nucleus, and the field frequency dictates its strongly anisotropic resonant shape. The predicted effect is especially strong for nucleation of pancake shaped nano-cavities in skin depth metallic layers. This significant modification of nucleation physics can have important implications in nano-photonics and optical recording. [http://dx.doi.org/10.1063/1.4737654]

Here, we predict a phenomenon of plasmonic mediated nucleation of nano-cavities in metallic layers that are penetrable to laser fields. The underlying mechanism is that the nucleated cavity provides a narrow plasmonic resonance that maximizes its polarizability. Adjusting the frequency and phase of resonance oscillations makes such cavities extremely energetically favorable, which changes the entire scenario of nucleation, strongly suppresses the nucleation barrier and shifts the phase equilibrium allowing nuclei that would not even be possible in zero field.

Non-photochemical acceleration of nucleation under laser or static electric fields has been observed in a number of systems.[1–4] Although the phenomenon was attributed to electric field induced lowering of the nucleation barrier, the critically important effect of frequency-dependent polarization, especially near plasmonic resonances, was overlooked. Here, we show that it strongly shifts the phase equilibrium and completely modifies the physics of nucleation for metallic phases.

Our consideration starts with the classical nucleation theory,[5,6] which accounts for the bulk μV and surface σA contributions to the free energy. With the addition of the term F_E to describe the electric polarization gain, the free energy is $F = F_E + \mu V + \sigma A$, where μ is the difference in chemical potential (per volume) due to cavity nucleation, σ is the surface tension, and V and A are the cavity volume and surface area, respectively. Our analysis below starts with the case of $\mu < 0$, corresponding to a metastable metallic system wherein nucleation is naturally expected. We then consider the case of a stable metal layer, $\mu > 0$, where cavities are energetically unfavorable in zero field.

For a static field, the polarization induced energy gain of a particle that nucleates in a dielectric material, with permittivity ϵ, can be represented as,[6]

$$F_E = -\epsilon \alpha E^2, \tag{1}$$

where α is the particle polarizability and E is the field strength. A subtle point here is that ϵ makes Eq. (1) different from the energy of a dipole in an external field; ϵ reflects the contributions from all charges in the system, including those responsible for the field. That factor was confirmed by several authors.[6–8] Equation (1) was originally obtained by integrating, over the entire space, the energy density difference caused by introduction of the particle. It must be modified for the case of dispersive media (metals), in which

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} + i\frac{\omega_p^2}{\omega^3 \tau}. \tag{2}$$

where ω is the field frequency, τ is the relaxation time, and $\omega_p = \sqrt{4\pi N e^2/m}$ is the plasma frequency with N being the electron concentration, m is the electron mass, and e is the electron charge. We assume, as usual, $\tau^{-1} \ll \omega \ll \omega_p$. The field energy density in strongly dispersive media is given by the Brillouin formula $(\partial(\omega\epsilon)/\partial\omega)(\bar{E}^2/8\pi)$ where the overline implies a time average [see, e.g., Eq. (80.12) in Ref. 9]. With the modification $\epsilon \to \partial(\omega\epsilon)/\partial\omega$, the derivation steps[6–8] leading to Eq. (1) yield,

$$F_E = -\frac{E^2}{2}\Re\left[\frac{\alpha\partial(\epsilon\omega)}{\partial\omega}\right], \tag{3}$$

where E is the field amplitude, $\Re$ represents the real part, and we have employed standard time averaging.[9] Since ω exceeds reciprocal nucleation times, the above time average represents an adiabatic contribution to the energy of the atomic subsystem.

We consider spheroidal particles, for which[10]

$$\alpha = \frac{V}{4\pi}\frac{\epsilon_p - \epsilon(\omega)}{\epsilon(\omega) + n(\epsilon_p - \epsilon(\omega))}. \tag{4}$$

Here, ϵ_p is the dielectric permittivity of the particle (cavity) and n is the depolarizing factor.

We start with the standard isothermal settings of a metastable system ($\mu < 0$) wherein cavities correspond to the thermodynamically stable phase, for example, in a liquid metal or in a metal supersaturated with vacancies and/or defects. The laser beam is normally incident on a metal and nucleation of small embryos takes place in its skin depth layer. In this part of our analysis, we assume a spherical particle shape typical of classical nucleation theory.

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Close to the resonance, $|\omega - \omega_r| \ll \omega_r$, using $n = 1/3$ for a sphere gives

$$\Re\left[\frac{\alpha\partial(\epsilon\omega)}{\partial\omega}\right] = R^3 c \frac{(\omega^2 - \omega_r^2) - a\omega_r^4/(2c)}{(\omega^2 - \omega_r^2)^2 + a\omega_r^4}, \tag{5}$$

where R is the radius of the sphere,

$$a = \left(\frac{1}{\omega\tau}\right)^2, \quad c = \frac{(\epsilon_p - 1)\omega^2 + \omega_p^2}{\epsilon_p + 2}, \quad \omega_r = \sqrt{\frac{2}{2+\epsilon_p}}\omega_p. \tag{6}$$

Assuming as usual $\omega\tau \gg 1$, we observe the resonance at $\omega^2 \approx \omega_r^2(1 - \sqrt{a})$ with a sharp minimum given by,

$$\Re\left[\frac{\alpha\partial(\epsilon\omega)}{\partial\omega}\right]_{min} \approx -\frac{R^3\epsilon_p\omega_p\tau}{2\sqrt{2+\epsilon_p}}. \tag{7}$$

This is by the quality factor $Q = \omega\tau \gg 1$ greater than the static polarizability ($\sim R^3$) of a metallic sphere.

The system free energy can be written as,

$$F = (E^2/2)[\Re(\epsilon\alpha)]_{min} + V\mu + A\sigma, \tag{8}$$

with $V = 4\pi R^3/3$ and $A = 4\pi R^2$. It reduces to its standard form of the classical nucleation theory with the renormalization,

$$\mu \to \mu_E = \mu + \delta\mu, \quad \delta\mu = -|\mu|\frac{E^2R_0^3}{W_0}\omega_p\tau\frac{\pi\epsilon_p}{6\sqrt{2+\epsilon_p}} \tag{9}$$

applicable both for $\mu < 0$ and $\mu > 0$. Here, we have introduced, for convenience, the radius and barrier of the classical nucleation theory,

$$R_0 = \frac{2\sigma}{|\mu|}, \quad \text{and} \quad W_0 = \frac{16\pi\sigma^3}{3\mu^2}.$$

Their ballpark values are $W_0 \sim 1$ eV and $R_0 \sim 1$ nm for the typical cases of nucleation in solids.[6] We observe from Eq. (9) that ac fields lower the barrier and radius of spherical void nucleation; the smallness of the effect is described by the dimensionless parameter $\xi = E^2R_0^3/W_0$ (see Fig. 1). A similar conclusion for dc fields has been long known.[6] A feature added here is the resonant nature of the ac field effect that is significantly amplified by the Q-factor.

Consider next the case of ac fields strong enough to distort the spherical geometry. It is known[12] that oblate spheroids remain stable with respect to elastic and electrical perturbations. Hence, we assume an oblate spheroid with the semi-major axis $R_\perp$ and semi-minor axis $R_\parallel$ directed perpendicular to and along the direction of beam propagation, respectively, (see Fig. 2). The depolarizing factor is given by[10]

$$n = \frac{1+\eta^2}{\eta^3}(\eta - \arctan\eta) \approx 1 - \frac{\pi}{2\eta} \equiv 1 - \delta n, \tag{10}$$

with eccentricity, $\eta = R_\perp/R_\parallel \gg 1$. Inserting Eqs. (2) and (10) into Eq. (4) and assuming $\omega \ll \omega_p$ yields,

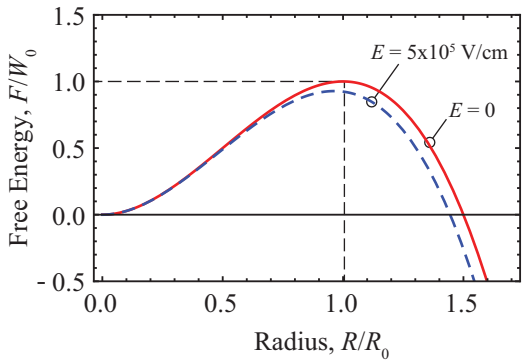

FIG. 1. Free energy of a spherical cavity in a metal. A slight lowering of the barrier requires $E = 4 \times 10^5$ V/cm at the plasmon frequency of $\omega_r = \sqrt{2/3}\omega_p$. Parameters values are typical for void nucleation in metals (see, e.g., Ref. 11): $\sigma = 1$ J/m^2, $R_0 = 0.5$ nm, $W_0 = 1$ eV, $\omega_p = 10^{15}$rad/s, and $\tau = 10^{-12}$ s, with $\epsilon_p = 1$.

$$\Re\left[\frac{\alpha\partial(\epsilon\omega)}{\partial\omega}\right] = -\frac{V\epsilon_p}{4\pi\delta n_\omega}\frac{(\delta n_\omega - \delta n) - a\delta n}{(\delta n_\omega - \delta n)^2 + a\delta n^2}, \tag{11}$$

where

$$\delta n_\omega = \frac{\epsilon_p\omega^2}{\omega^2(\epsilon_p - 1) + \omega_p^2} \approx \epsilon_p\frac{\omega^2}{\omega_p^2} \ll 1.$$

The polarizability exhibits resonance behavior near $\delta n \approx \delta n_\omega$ with a sharp minimum when,

$$\delta n \approx \delta n_\omega(1 - \sqrt{a}). \tag{12}$$

The corresponding value is

$$\Re\left[\frac{\alpha\partial(\epsilon\omega)}{\partial\omega}\right]_{min} \approx -\frac{V}{8\pi}\frac{\omega\tau}{\epsilon_p}\left(\frac{\omega_p}{\omega}\right)^4. \tag{13}$$

Equation (12) shows that the aspect ratio of the nucleated void is governed by the frequency,

$$\frac{R_\parallel}{R_\perp} \approx \epsilon_p\frac{\omega^2}{\omega_p^2}. \tag{14}$$

$R_\perp$ remains to be determined by minimizing F.

The resonant frequency ω expressed in Eq. (14) through the aspect ratio is known as the plasmonic resonance frequency which describes collective oscillations of quasi-free

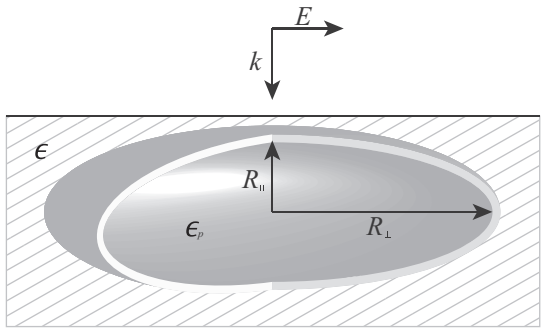

FIG. 2. Oblate spheroidal cavity of permittivity ϵ_p, semi-minor axis $R_\parallel$, and semi-major axis $R_\perp$ embedded in a thin metal film of permittivity ϵ.

electrons; it has been experimentally observed in light scattering by nanoparticles.[14] As a simple qualitative argument, consider an oblate spheroidal cavity with $\epsilon_p = 1$. Shifting the positive and negative components in its surrounding plasma over small distance, $x \ll R_\perp$ along $R_\perp$, deposits charges $q \sim R_\parallel R_\perp xNe$ on the two halves of the spheroid. Each of them exerts forces $\sim qe/R_\perp^2$ on individual electrons on the opposite side. Interpreting the latter as the restoring forces $m\omega^2 x$ yields the resonant frequency $\omega \sim \omega_p\sqrt{R_\parallel/R_\perp}$, consistent with Eq. (12).

Note that $|[\Re(\epsilon\alpha)]_{min}|$ in Eq. (13) is by the Q-factor greater than the static polarizability of a metallic *prolate* spheroid of the reciprocal aspect ratio,[4,9] $\alpha \approx (V/8\pi)(R_\parallel/R_\perp)^2$, where $R_\parallel/R_\perp \gg 1$. In the mean time, slightly modifying the above analysis shows that a prolate spheroidal cavity in a metal does not possess any strong polarizability. This can be attributed to strong metal screening of the polarization charges induced at the spheroid poles. The case of plasmonic-driven nucleation of a metal prolate spheroid in a dielectric medium, which will be presented elsewhere,[15] is characterized by a smaller resonant effect than predicted here.

As illustrated in Fig. 3, the minimum in $\Re[\alpha\partial(\epsilon\omega)/\partial\omega]$ of Eq. (13) is so sharp that all other terms containing δn in the free energy of Eq. (8), with $\mu > 0$, can be evaluated at $\delta n = \delta n_\omega$. The volume and area are then,

$$V = 4\pi R_\perp^3/3\eta \approx 8R_\perp^3\delta n/3, \quad \text{and} \quad A = 2\pi R_\perp^2.$$

Normalizing the free energy with respect to the classical barrier, it takes the form

$$\frac{F}{W_0} = \frac{4}{\pi}\frac{R_\perp^3}{R_0^3}\frac{\epsilon_p\omega^2}{\omega_p^2}\left[-\frac{E^2R_0^3}{24W_0}\left(\frac{\omega_p}{\omega}\right)^4\frac{\omega\tau}{\epsilon_p} + \frac{\mu}{|\mu|}\right] + \frac{3}{2}\frac{R_\perp^2}{R_0^2}, \quad (15)$$

Comparing this with Eq. (15) shows that the field effect is much stronger for highly anisotropic oblate spheroids than for spheres when $\omega \ll \omega_p$.

The instability takes place when the bulk chemical contribution [second term in Eq. (9)] is smaller that the field term, i.e., when

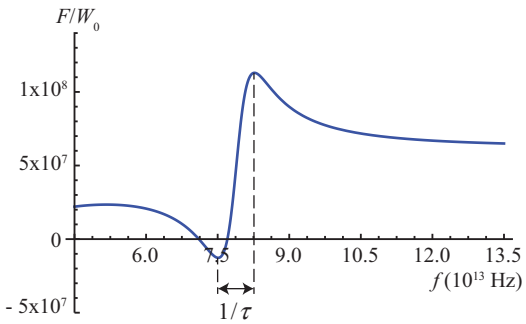

FIG. 3. Normalized free energy of an oblate spheroidal cavity vs. field frequency $f = \omega/2\pi$, with $E = 3 \times 10^3$ V/cm. The sharp resonance of width $1/\tau$ determines the aspect ratio $R_\parallel/R_\perp \approx (\omega/\omega_p)^2 \approx 10^{-4}$. Numerical values are the same as those used in Fig. 1.

$$E > E_\omega \equiv E_c\frac{1}{\sqrt{\omega\tau}}\frac{\omega^2}{\omega_p^2}, \quad E_c \equiv 2\sqrt{\frac{6W_0\epsilon_p}{R_0^3}}. \quad (16)$$

Assuming the above ballpark parameter values and $\epsilon_p = 1$ yields the characteristic field $E_c \sim 10^8$ V/cm. However, the other multipliers can easily make the right hand side in the inequality of Eq. (16) much lower, taking it down to say, 1 kV/cm, which corresponds to low power density lasers $P \sim 10$ mW/μm^2.

Minimizing the free energy with respect to $R_\perp$ yields the nucleation radius and barrier,

$$R_{\perp,0} = R_0\frac{\pi\omega_p^2}{2\omega^2\epsilon_p}\left[\frac{E^2}{E_\omega^2} - \frac{\mu}{|\mu|}\right]^{-1} \gg R_0 \quad (17)$$

and

$$W \approx W_0\left(\frac{E_c}{E}\right)^4\left(\frac{\omega}{\omega_p}\right)^2\frac{1}{(\omega_p\tau)^2} \ll W_0 \quad (18)$$

when $E \gg E_\omega$ regardless of the sign of chemical potential difference μ. We conclude that plasmonic nucleation involves nucleation barriers much lower than the typical nucleation barriers in solids and results in highly flattened pancake shaped cavities even when such cavities are not energetically allowed in zero fields. For comparison, resonant nucleation of metal nanoparticles ("inside-out" with respect to this work) can be shown[15] to have a barrier that is higher by the factor of $\omega_p/\omega \gg 1$ than W in Eq. (18). It is our conclusion that nucleation of nano-voids is facilitated by plasmonic resonances the most among other conceivable cases.

As a prototype system to which the above theory applies, we consider again a metal close to a phase transition at temperature T_m, yet stable. This enables one to estimate its chemical potential as $\mu = \mu_0(1 - T/T_m)$. Correspondingly, the classical nucleation radius and barrier become

$$R_0 = R_{00}(1 - T/T_m)^{-1}, \quad W_0 = W_{00}(1 - T/T_m)^{-2}, \quad (19)$$

and $E_c = E_{c0}(1 - T/T_m)^{1/2}$, where R_{00}, W_{00}, and E_{c0} are estimated as the atomic scale values. This allows macroscopically large R_0, consistent with the classical nucleation theory.

Using the latter relations and assuming that the first term in parenthesis of Eq. (17) dominates, one gets

$$W = W_{00}\frac{\pi^2}{8}\frac{1}{(\omega\tau)^2}\left(\frac{\omega}{\omega_p}\right)^4\left(\frac{E_{c0}}{E}\right)^4. \quad (20)$$

The nucleation barrier turns out to be temperature independent, in striking difference with the classical nucleation theory, which predicts a diverging nucleation barrier W_0 in Eq. (19).

We now briefly discuss possible implications of our theory. A metal close to a phase transition would be most suitable for experimental verification. Since the cavities lie within the skin layer depth, they are optically accessible and can be identified via the unique features of oblate spheroids in light scattering and absorption.[16]

For stronger fields, $R_\perp$ and $R_\parallel$ in Eqs. (14) and (17) can shrink below the atomic length scale, beyond the range of the proposed macroscopic description. The prediction of energy gain due to resonant cavity nucleation remains valid then in the range of macroscopic post-nucleation dimensions, though the transitions rates to the lower energy state are difficult to estimate.

We note the observed formation of pancake shaped voids in metal films under moderate power density ($P \sim 1$ W/μm^2) laser beams.[13] Similar nanovoids have been explained by thermal instabilities and recrystallization.[17] Laser ablation[18] is observed for $P \gtrsim 10$ W/μm^2. The effects proposed in this letter can be identified under much lower power densities $P \lesssim 1 - 100$ mW/μm^2 that are insufficient to cause melting.

The possibility of creating all-metal nano-cavities with well controlled shapes opens a venue towards high Q-factor resonators, important in nano-optics and capable of efficient lasing.[19–21]

Our theory can help to elucidate the physics of optical recording in DVD and related technologies where information is kept in the form of small dielectric amorphous bits embedded in a semi-metal crystalline film (polycrystalline $Ge_2Sb_2Te_5$, etc.). The mainstream understanding has been that such metastable bits appear due to quenching of laser generated melted spots. However, recent experimental work[22] has shown that the process does not evolve through the melt. Our predicted nucleation of dielectric cavities suggests that the observed dielectric bits in semi-metal films can be created under laser irradiation (and stay as metastable inclusions afterwards) simply because they are more energetically favorable. A theory of nucleation and growth of such bits can be used to optimize optical recording with respect to the material and laser beam parameters.

In conclusion, we have predicted a new class of nucleation phenomena where the phase transformation energy is supplied by the electromagnetic field in resonance with plasmonic oscillations. It may have important practical implications. More work is called upon to describe the growth stage of such resonant cavities and relate them to the experimental observations.

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