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THEORETICAL STUDY OF OPTICAL PROCESSES DUE TO STRUCTURAL PHASE TRANSFORMATION AT Ga/Si INTERFACE

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Interesting results have been obtained for optical processes related to light induced structural phase transformation for a gallium nanoparticle film deposited on a transparent dielectric substrate. Theoretical calculations of reflectance, transmittance, plasma frequency and optical transition rate have been carried out. The effective medium theory has been used to investigate the nonlinear response of film as a consequence of thermal and non-thermal light metallization effects. The results obtained are in agreement with the available experimental data.

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1. Introduction

We are entering the age of integrated photonic devices for signal and information processing when planar waveguides and photonic crystal structures are being intensively investigated as primary solutions for guiding lighting such devices[1]. There may however be another means of making highly integrated optical devices, with structural elements smaller than the wavelength, enabling strong guidance and manipulation of light using metallic and metallo dielectric nanostructures. An optically induced phase transitions in nanoscale layers of gallium at an interface with glass can be used to achieve a large reflective nonlinearity [2]. In this work, we report the light driven 'surface melting' effect in Ga nanoparticles, giving reflective and transmissive nonlinear responses which are consistent with predictions based on an effective medium theory for the optical properties of a layer of closely packed nanoparticles [3]. Depending on the fact that light can be used to induce a reversible transformation between two phases of gallium (α and liquid), thermal effects such as variation in metallic layer's thickness with increase in temperature as well as increase in reflectivity of the film has been theoretically investigated. The non-thermal model relies on the unique structure of α-gallium in which molecular and metallic properties coexist. The nonlinear response of the nanoparticle film in this case has been studied using the standard equations for populations in a multilevel system and thin film formulas [4]. Calculations for the non-thermal model are based on the dependence of effective dielectric constant of the film at interface on the nanoparticle aspect ratio.

Metallic Gallium is a uniquely suitable material for this application. It is known for its polymorphism [10]. In α-gallium, the stable 'ground-state' phase molecular and metallic properties coexist - some interatomic bonds are strong covalent bonds, forming well defined Ga_2 dimers (molecules), and the rest are metallic bonds [11]. The structure is highly anisotropic, with much better thermal and electrical conductivity in the 'metallic planes' than along the covalent bonds. Remarkably, α-gallium has a very low melting point, 29.8◦C. The covalent bonding leads to a strong optical absorption peak centered at 2.3 eV and spreading from approximately 0.68 eV (_310

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nm) to the mid-infrared part of the spectrum. Optical properties of the α-Ga and more metallic phases, metastable at normal conditions, are greatly different in terms of the dielectric coefficients of liquid gallium and solid gallium. The metallic metastable phase (quasi-melt) may be achieved by simple heating, or by light absorption through a nonthermal "optical melting" mechanism via destabilization of the optically excited covalent bonding structure [7].

Whatever the mechanism of phase transition is, it is a surface mediated effect and develops as propagation of the new metallic phase from the surface into the bulk of the semiconductor-like α-phase. As the phase transition only involves a few tens of atomic layers of gallium at the interface, it is highly reproducible and fully reversible and could run for millions of cycles without noticeable changes. High quality gallium interfaces with silica may be achieved using various techniques, from squeezing molten gallium to ultra-fast pulsed laser deposition[12].

2. Theoretical analysis

Experimentally, the nonlinear optical response of the gallium-silica interface has been studied by the use of pump-probe reflectivity measurement technique [5]. Observations depict that the sample's reflectivity changes continuously at the metal glass interface just below the metal's melting point. This observation suggests that a surface wetting layer of a different (more reflective) phase is formed at the interface. Theoretical analysis of the results obtained experimentally can be performed using the concept of surface-driven dynamic coexistence of structural forms in Ga [6]. It is found that the Ga-silica interface when exposed to an optical excitation give rise to a new phase that appears first at the surface and then grows inwards with increasing temperature. It can be assumed that the nanoparticle transforms to a new phase, solid or liquid, but only partially, through an increase in the skin layer thickness. It is a reversible transformation which means that as soon as the optical excitation is withdrawn, the particle recrystallize back into the initial phase. At a high level of optical excitation, above a threshold the particle is transformed completely to a new phase with an irreversible change in its optical properties [7].

Initially, we assume a layer of α- gallium with relatively low reflectivity to be deposited on the silica substrate. When exposed to a laser beam of appropriate intensity a thin transient, more metallic layer is formed at the Ga-silica interface. The reflectivity and thickness of this transient layer strongly depends on the intensity of applied light. Using the light-induced metallization model [8] and measurements of effective thermal capacity at gallium-vacuum interface [8], we can represent the temperature dependence of metallic layer's thickness as:

$$D = D_0 + \Delta \exp[-\mu(T_m - T)] \tag{1}$$

Where, Δ and μ are fitting parameters and T_m is the melting temperature of gallium~30°C. Assuming μ to be intensity dependent, we plot a graph between D and increasing temperature (fig.1) which show that the metallic layer's thickness changes drastically near the gallium's melting temperature giving rise to a completely new metallic phase. Moreover, using this dependence of metallic layer's thickness, we study the variation in layer's reflectivity with temperature (fig.2) using the standard thin film formulas [4].

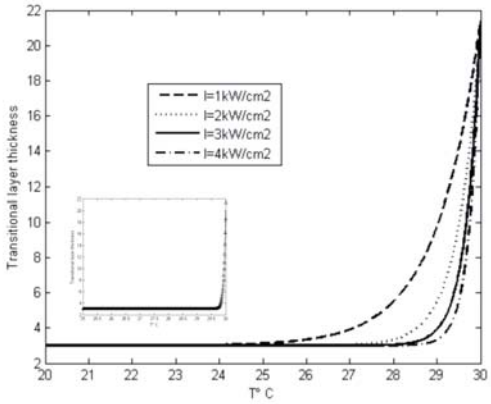

Fig. 1. Variation of metallic layer' thickness with temperature

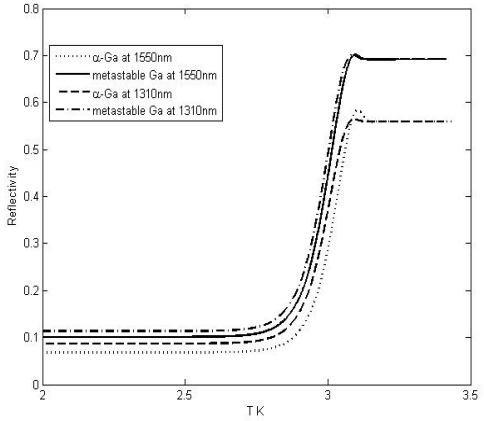

Fig. 2. Variation of reflectivity at the interface with temperature

Again, if we consider the transient state of gallium as a homogenous mixture of two phases i.e the α-Ga and liquid gallium, the transient dielectric function at the interface can be obtained using the Maxwell-Garnett effective medium theory [10], as follows:

$$\varepsilon_{transe} = \varepsilon_{\alpha-Ga}[1 + \frac{3C(\varepsilon_{liq-Ga} - \varepsilon_{\alpha-Ga})}{\varepsilon_{liq-Ga} + 2\varepsilon_{\alpha-Ga} - C(\varepsilon_{liq-Ga} - \varepsilon_{\alpha-Ga})}] \tag{3}$$

Where, C is the volume fraction of the liquid phase formed in crystalline α-Gallium and $\varepsilon_{\alpha\text{-}Ga}$ is the dielectric function of α-Ga and $\varepsilon_{liq\text{-}Ga}$ is the dielectric function of liquid-Ga.

Using the above formula we can study the variation of dielectric function ε_n of the mixture of phases ε_{transe} with C (fig.3). The concentration of liquid gallium in the transient phase can be calculated by applying this formula to the modulus of the dielectric function $|\varepsilon|=(\varepsilon_1^2+\varepsilon_2^2)^{1/2}$. Dielectric function of gallium for α and liquid phase at various wavelengths is shown in table 1.

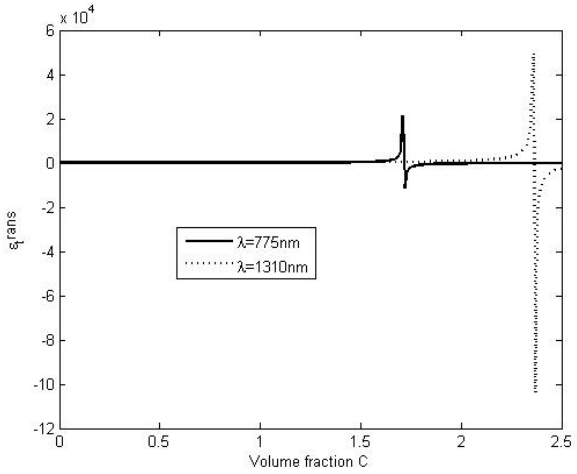

Fig. 3. Variation of transient dielectric function with volume fraction c at different wavelength

Table 1.

Wavelength λ in nm	α-crystalline state		Liquid state	
	ε_1	ε_2	ε_1	ε_2
775nm	-7.05	12.79	-66.00	34.93
1310nm	-25.9	39.7	-115.3	98.4
1550nm	-1.29	21.55	-12.18	38.11

It is found that α- gallium is a molecular crystal with a combination of molecular and metallic characteristics [10] while liquid gallium [12] is a free electron-like metal. Using the both crystalline and liquid state, we can calculate the plasma frequency ω_p^2/ω^2 and the electron-phonon effective collision frequency (optical rate) v_p/ω expressed in units of ω as follows [13]:

$$\left(\frac{\omega_p}{\omega}\right)^2 = (1-\varepsilon_1)\left[1+\left(\frac{\varepsilon_2}{1-\varepsilon_1}\right)^2\right]; \text{ and } \frac{v_{opt}}{\omega} = \frac{\varepsilon_2}{1-\varepsilon_1} \tag{4}$$

The values of these constants calculated at different wavelengths for α and liquid phase is shown in table 2.

Table 2

Wavelength	α-crystalline phase		Liquid gallium	
	ω_p^2/ω^2	ν_p/ω	ω_p^2/ω^2	ν_p/ω
λ =775nm	28.4	1.59	85.2	0.521
λ =1310nm	85.9	1.47	199.38	0.846
λ =1550nm	28.37	1.58	123.31	2.89

These two parametric forms describe well the experimentally observed optical properties of both α-gallium and liquid gallium in equilibrium conditions at 775nm and 1550nm respectively. It is clear that the plasma frequency and the electron-phonon collision rate achieve higher values as soon as a new phase is formed and this give rise to the observed reflectivity changes at the gallium-silica interface. The plot of both these parameters with time is shown in fig.4 and 5.

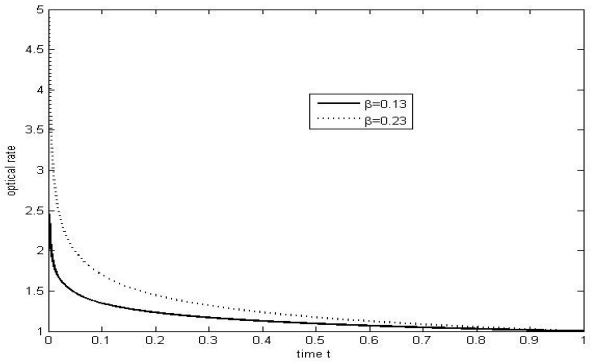

Fig. 4 : Variation of optical rate with time (ns)

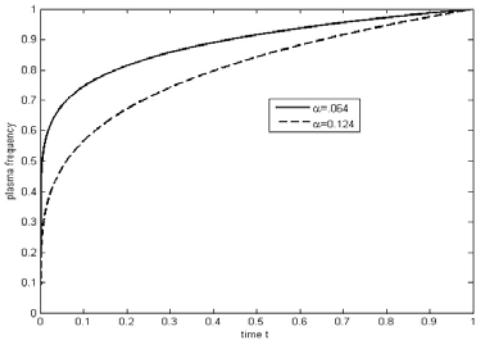

Fig. 5. Variation of plasma frequency with time in ns

The nonthermal model relies on the unique structure of α-gallium in which molecular and metallic properties coexist: Some bonds are covalent, forming Ga_2 dimers and the remaining bonds are metallic. The model assumes that absorption of light at a particular wavelength (nm) results in highly localized excitation of gallium dimers from the bonding (*b*) to the antibonding (*a*) state, reducing the stability of the surrounding crystalline cell. The cell subsequently undergoes a transition to a new metastable configuration (crystalline or disordered), creating a microscopic inclusion of the new phase (*m* state of the cell). From the standard equations for populations in a multilevel system one can now calculate the relative number density of crystal cells in the *m* state sustained by the presence of light:

$$\frac{n_m}{n} = \left(\frac{\gamma_m}{\gamma_b}\right) \frac{\Gamma}{\left[2\Gamma + \tau^{-1} + \gamma_m\left(1 + \Gamma/\gamma_b\right)\right]} \tag{5}$$

Where, n is the number density of cells, γ_m and γ_b are correspondingly, transition rates from the excited (a) to the metastable (m) state and from the metastable to the ground (b) state, and τ is the lifetime of the excited state.

$$\Gamma = \frac{(1-R)I\alpha}{h\nu n} \tag{6}$$

Where, R and α are, respectively, the optical reflection and absorption coefficients of α-gallium and I and ν are the intensity and the frequency of incident laser beam. The metallic layer's thickness for the nonthermal model can be obtained by substituting $\mu_0(1 - n_m/n)$ in place of μ in equation (1) i.e;

$$D = D_0 + \Delta \exp[-\mu_0\left(1 - n_m/n\right)(T_m - T)] \tag{7}$$

The variation is shown in Fig. 1 as inset.

If the film is considered to be a monolayer of small particles distributed on the surface of a transparent substrate, we can derive an expression for the effective dielectric constant of the nanoparticles at the interface, using the Maxwell-Garnett Effective Medium Theory [3]. If it is assumed that the particles grow preferentially across the surface of the substrate, the rate of deposition of nanoparticles is given by [13]:

$$\frac{dD}{dt} = 2G\left(\frac{r^2}{\pi h}\right)\frac{1}{D} - 2\left[\beta G\left(\frac{r^2}{\pi h}\right)\frac{1}{D} + \nu d \exp\left(\frac{-E_m}{k_b T}\right)\right]\frac{n_m}{n} \tag{8}$$

Where G is the nanoparticle growth(nm/min), r is mean distance between the particles, h is the height of nanoparticle, D is nanoparticle diameter in nm, ν is vibration frequency of covalent bonds, E_m is energy of metastable state, T is nanoparticle temperature, and $\beta = 1 - \sigma_m/\sigma_g$, where σ_m and σ_g are the adsorption coefficient in metastable and ground state respectively. Moreover, the local field for the nanoparticles taking into account their electrostatic dipole interaction is given by[14]:

$$L(\omega, D) = \left(1 + \left[\varepsilon_{eff} - 1\right]\left[\frac{1 - \pi(D/2r)^2}{2\sqrt{1+\gamma^2}}\right]\right)^{-1} \tag{9}$$

Where, ε_{eff} is the effective dielectric constant of nanoparticles given by[3]:

$$\varepsilon_{eff} = \varepsilon_{ext}\left(q\frac{(\varepsilon_{\text{int}} - \varepsilon_{ext})}{\varepsilon_{ext} + F(\varepsilon_{\text{int}} - \varepsilon_{ext})} + 1\right) \tag{10}$$

Where, q is volume filling factor of nanoparticles and F is the effective geometrical factor of nanoparticles depending on their aspect ratio γ. Taking, into account the optical conductivity spectrum of α-gallium [15] we can substitute G=0.3nm, r=80nm, h=2nm, ν=3.4 $\times 10^{13} s^{-1}$, E_m=0.289 eV, d=0.76nm, T=100K for the plot of change in nanoparticle diameter D with deposition rate(fig.6) and for the plot of $|L|^2$ against nanoparticle aspect ratio γ(fig.7).

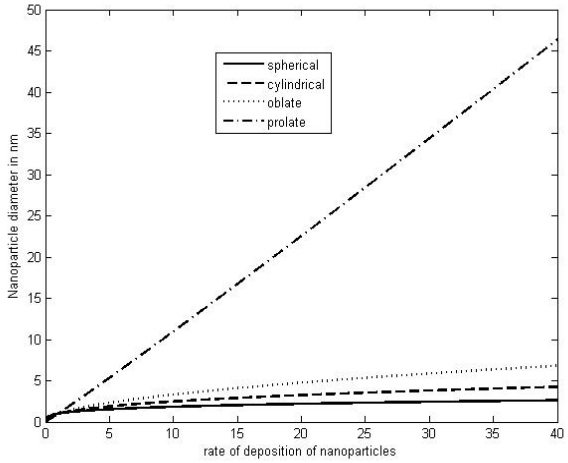

Fig. 6: Variation of nanoparticle diameter(nm) with rate of deposition

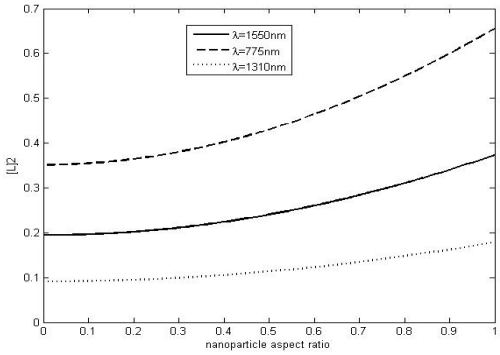

Fig. 7. Variation of $|L|^2$ with nanoparticle aspect ratio

3. Results and discussion

The variation of metallic layer's thickness with temperature at different intensities is shown in fig.1. The plot shows that the thickness changes just below the melting point of the metal-solid interface which strongly suggest that a surface wetting layer of a different(more metallic) phase is formed, a phenomenon that was previously reported at liquid-crystal-glass and vacuum-metal interfaces. Thermodynamically, we can conclude that the surface energy of the wetting phase at a glass interface is lower than that of α-gallium. Moreover, as the thickness of this phase depends on temperature and the reflectivity is also a function of temperature, we can estimate that the reflectivity of the interface increases according to the thickness of the layer.

Fig.2 represents the dependence of interface reflectivity on temperature and incident light intensity for λ=1310 nm & λ=1550 nm. The theoretical measurements are based on thin film formulas for reflectivity. The dielectric coefficients of both the phases are taken as ε_α = -1.29 – *i*21.55 and ε_m = -12.18 – *i*38.11 respectively. Using $N_\alpha^2 = \varepsilon_\alpha$ where $N_\alpha = n_\alpha - ik_\alpha$ is the complex refractive index of the material we find $n_\alpha = 3.186$ and $k_\alpha = 3.382$. Similar calculations for the metastable phase has been performed and the values obtained are $n_m = 3.73$ and $k_m = 5.108$ respectively. It is observed that the reflectivity of α-gallium is ~0.55 for λ==1310 nm & 1550 nm and it is found to be ~0.7 for metastable phase. At a certain temperature T_a below the phase transition point T_1 the influence of light on the surface layer's thickness becomes apparent as optical excitation changes the reflectivity of the film. With increasing temperature or level of optical excitation, the surface layer's thickness increases until the transformation of the core to the

"surface" phase is completed. When at T_1, the core of the particle is fully consumed by the new phase, the nanoparticle becomes stable against return to the old phase. This process is reversible for a particular temperature range between T_a and T_1.Theoretically this range lies between 275°C and 302°C. Experimental results show the range to be between 250°C and 350°C [2]. The theoretical model presents correctly positioned peaks for reflectivity of film and the discrepancies between the theoretical and experimental results may be due to defect or inclusion in the new phase that change the optical properties of the host phase at temperatures far below its transition point. This is a reversible process, which give rise to a remarkable amount of nonlinearity at the interface. This nonlinearity can be used to operate an all-optical switch, where an optical signal is used to control the intensity of another beam. The nonlinearity growth with temperature is observed maximum near the transition temperature (melting point).

Fig.3 represents the variation of dielectric function of the transient phase with volume fraction C of liquid gallium It is found that initially the dielectric function ε_{trans} varies smoothly with C but at C~2.5 there is a sudden fall in the curve and then it acquires it's original shape but with some decrease in value of dielectric function of the transient phase. This show that the light-induced surface metallization effect in α-gallium give rise to a new phase (metastable phase) which exhibit entirely different dielectric properties. It is also observed that at small wavelengths the metastable phase is achieved for low value of volume fraction.

The variation of electron-phonon collision rate (optical rate) and plasma frequency with time in ns is shown in fig.4 and fig.5. It is evident from the graphs that the optical rate as well as the plasma frequency changes in the first 1ns after the laser beam of intensities 1 to 4KW/cm^2 is applied. However, neither the electron-phonon collision rate (optical rate) nor the plasma frequency reaches the values for liquid gallium in equilibrium conditions. The existence of two time stages with different slopes is also evident in the first 0.1 to 0.4ns range followed by a slower evolution over a period of tens of ns.

For a monolayer of nanoparticles at silica substrate, the variation of nanoparticle diameter as a function of deposition rate is shown in fig.6 for different nanoparticle shape and size. The result is more pronounced for prolate spheroids then compared to spherical, cylindrical and oblate. Thus, it may be estimated that for prolate spheroids with higher aspect ratio the diameter achieves a higher value. However, the growth rate is always positive and the nanoparticle does not achieve a stationary diameter. Fig.7 represents $|L|^2$ as a function of aspect ratio at different wavelengths. It is clear from the graph that $|L|^2$ increases progressively with the aspect ratio γ at λ=1310nm. It leads to a conclusion that the growth of large nanoparticles is faster than smaller ones.

The results obtained for the non-thermal model are consistent with those obtained for the thermal model. The increase in metallic layer's thickness with rising temperature can be studied using equation (7). According to this model, the metastable phase has a more metallic character, and hence a higher reflectivity than α-gallium. Once the optical stimulation is removed it relaxes back to the stable α-gallium phase. It is shown in [11], that the molecular character of α-gallium leads to a broad absorption band extending from 0.8-4 e V (i.e 310-1550nm). Absorption of quantum with energy energy within this band leads to breaking of the typical covalent bonding of α-gallium lattice. The crystal then tends to jump into a new phase, one more energetically favourable. Thus, it can be assumed that the free-electron structure is of more metallic character than α-gallium, resulting in a higher reflectivity.

4. Conclusions

The present work investigated the nonlinear optical processes that occur at the Ga-silca interface using the thermal and nonthermal light metallization effects as a result of intense light falling on the ga materia . The effective medium theory along with the models of thermal and nonthermal metallization due to structural phase transformation is used to explain the derived results. It is concluded that thickness changes just below the melting point of the metal-solid interface which strongly suggest that a surface wetting layer of a different (more metallic) phase is formed. At a certain temperature T_a below the phase transition point T_1 the influence of light on

the surface layer's thickness becomes apparent as optical excitation changes the reflectivity of the film. The light-induced surface metallization effect in α-gallium give rise to a new phase (metastable phase). The optical rate as well as the plasma frequency changes in a very short time with beam intensities upto $4KW/cm^2$. The nanoparticle diameter achieves a higher value for oblate spheroids and local field intensity increases progressively with increasing aspect ratio at λ=1310nm. The results are in conformity with the experimental data obtained by other workers.

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