Nanoscale Sensing Glass Transition of Nanoconfined Polymers Through Thermoplasmonics

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In the conditions of the modern desire for miniaturization of optoelectronic and photonic devices, the element base of which includes nanosized polymeric materials, the control of their local temperature of phase transitions plays a decisive role. This parameter is an indicator of the temperature stability of the polymer material, which means the stable operation of the device itself. A well-known fact is the anomalous behavior of the glass transition temperature associated with a decrease in the size of the polymer material at the nanoscale. However, most of the methods of determination of the glass transition temperature known today need macroscopic heating of the sample, which can lead to its irreversible destruction of its geometry. As a result, new approaches and methods are required to ensure the registration of the local temperature of phase transitions.

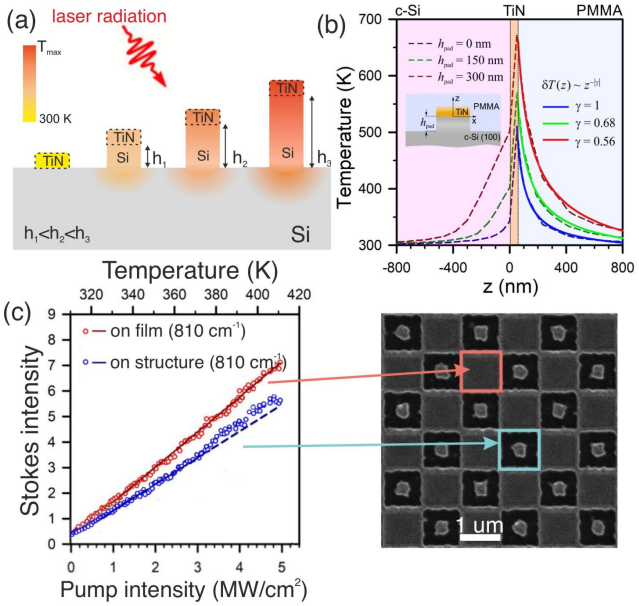

Figure 1: (a) Scheme of enhancement of optical heating of titanium nitride nanostructures using a nanostructured thermostat surface; (b)FEM calculated temperature profiles of a 200 nm TiN antenna for different heights of Si nanostructures; (c) Dependence of the Stokes intensity of the 810 cm^{-1} vibrational mode on the pump intensity and temperature

We propose to detect the local glass transition temperature using light-induced heat at the nanoscale. Such heating can be generated by plasmonic nanostructures under the action of light under plasmon resonance conditions [1]. However, the results of experiments and numerical simulations showed that the increased heat generated by the nanostructure can be dissipated into the substrate with high thermal conductivity, and as a result, the heating of the nanostructure will be negligible. We propose a new approach to the creation of controlled heating of plasmonic nanostructures, which is based on the nanostructuring of the surface of the substrate (thermostat). This is achieved by creating structures - parallelepipeds stacked on top of each other. The dimensions of the titanium nitride nanostructure are 200x200x50 nm, and the size of the silicon structure is 200x200 nm with a variable height (Figure 1a). The entire system is illuminated by low-intensity continuous laser radiation 633 nm (5 MW/cm^2). The silicon nanostructure limits heat dissipation since the heat in it spreads in one direction, namely along the height. Using Raman thermometry (silicon line shift) [2] and numerical simulation methods, we demonstrate that the higher the structure of silicon, the higher temperatures are achieved. Thus, the height of the silicon nanostructure sets the maximum heating temperature, and the temperature can be controlled by changing the laser radiation intensity. It means that the creation of enhanced heating of metal nanostructures, which will initiate the glass transition of the polymer, is possible due to the nanostructured surface of the thermostat.

As a nanosized polymer, we consider a thin PMMA polymer film (Tg=110°C). Using numerical simulations, we determine the optimal silicon structure height (220 nm) that allows heating a thin PMMA film above the glass transition temperature (Figure 1b). The glass transition temperature was determined using Raman spectroscopy. To do this, we built the dependence of the intensities of the vibrational modes

of the PMMA polymer on the pumping intensity (0–5 MW/cm2) of the polymer, which lies on the array of structures. The glass transition temperature is defined as the point at which one linear trend changes to another (Figure 1c). The change in the linear trend is due to the fact that upon achieving the Tg point, the light-to-heat energy goes to unfreeze the segmental mobility of the polymer backbone. The value of the glass transition temperature determined by our proposed method is in good agreement with the glass transition temperature range of the PMMA polymer. Thus, we conclude that the structures provide a unique opportunity to study the local glass transition temperature of nanosized polymers using Raman thermometry and thermoplasmonics methods.

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References

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