Chapter 10

Nano-ripple semiconductors as target for ultra-short laser absorption

Surface structuring with lasers is a highly competitive method due to its capability of making fast and easy to implement changes in the structure design [224]. Compared to the picosecond and nanosecond laser pulses, the energy in a femtosecond pulse can be precisely and rapidly deposited in a solid material with fewer thermal effects [225]. Therefore, the femtosecond lasers are widely used in micro-fabrication in transparent materials, metals and semiconductors for applications like modifying the optical properties of the surface [226], improvement of photovoltaic devices by increasing their effective surface area and in turn increasing the response and conversion efficiency [227]. The other applications include modification inside refractive index of bulk materials for fabricating photonic devices, optical data storage, and bio-photonic components [228-230].

Mid-IR femtosecond laser radiation is generally used for the generation of surface ripples, also known as laser-induced periodic surface structures (LIPSS). Various mechanisms have been proposed to explain the nano-ripple formation. Initially, it was thought to be the result of the interference between incident laser light and the scattered light from the surface roughness [231]. However, if this mechanism were to be true, nano-ripple width should always be of the order of the incident laser light wavelength, whereas in many experiments very narrow ripple formation has been observed. For example, Ozkan et al [232] found that ripples resulting from 248 nm femtosecond laser irradiation of thin diamond films had a period varying between 50–100 nm. Yasumaru et al [233] reported formation of ripple patterns with mean periods of 100–125 and
30–40 nm on TiN and diamond-like carbon after irradiation with 800 and 267 nm femtosecond pulses, respectively. To explain the nano-ripple formation in the case of metals, the surface plasmon created during initial random surface heterogeneities is considered [234]. In dielectrics, the coupling of the electron plasma wave and incident laser explains the observed periodic structure in glass [235]. Other proposed mechanisms for ripple formation are self-organization [236], Coulomb explosion [237], influence of second harmonic generation [238], anisotropic local field enhancement invoking nano-plasmonics [239], etc.

In this chapter, a study of surface nano-ripple formation on different band gap semiconductors is presented. A parametric study of the ripple formation with different laser parameters and ambient media is done with the objective of identifying conditions of forming narrow period ripples. Nano-ripples were formed using a Ti-sapphire laser with 8 mJ energy, 45 fs pulse duration and 800 nm wavelength (1.56 eV) at a fluence in the range of ~ 100 mJ/cm$^2$ – 1J/cm$^2$. The effect of the number of laser shots, the angle of incidence, polarisation of the laser, fluence, incident laser wavelength, band gap and ambient medium has been studied. Depending upon the experimental parameters, the nano-ripple sizes varied in the range of $\lambda/9$ to $\lambda$. Narrow nano-ripples are formed from wide band gap semiconductors. The width of the nano-ripples also decreases with the laser wavelength and the laser fluence. The observation of high and low spatial frequency ripples in different conditions is explained considering the transient metallic nature of the semiconductor surface on irradiation with intense femtosecond pulses. The surface eventually supports the surface plasmon excitation, which interferes with incident laser light for ripple formation. We attribute the very delicate dependence of ripple period with incident laser parameters to the critical role of electron density. The finding helps identifying suitable band gap
materials and laser parameters for obtaining nano-ripple period considerably small compared to the incident laser wavelength.

10.1 Experimental setup

For studying the nano-ripple formation from ultra-short laser pulse irradiation of semiconductor materials of different band gaps, the following semiconductor materials of narrow (< 1.5 eV, which is the energy of the incident 800 nm photon) band gap: InAs (0.36 eV), GaAs (1.42 eV), InP (1.35 eV), and wide (> 1.5 eV) band gap materials like GaP (2.3 eV), GaN (3.4 eV), SiC (3.37 eV), ZnSe (2.82 eV) were used. Multiple laser shots from a Ti-sapphire laser with 8 mJ energy, 45 fs pulse duration, and 800 nm wavelength were focused in air on the semiconductor wafers at a fluence in the range of ~ 100 mJ/cm$^2$ – 1J/cm$^2$, i.e. around the plasma formation threshold. Using a BBO crystal, the second harmonic (400 nm) of the 800 nm laser beam was also used to study the influence of the laser wavelength on the ripple formation, while keeping the other parameters same. The effect of the number of laser shots, the angle of incidence, the polarisation of the laser, the fluence, the band gap, and the ambient medium was studied. The spatial features of the laser treated semiconductors were characterized using SEM (Philips XL30CP). The schematic of the experimental setup was already described in chapter 2.

10.2 Experimental results

Figure 10.1 shows the surface morphologies resulting from the irradiation of a GaP wafer by femtosecond pulses with two different polarisations and in two different spatial regions. Figure 10.1a shows the formation of spherical nano-particles (~100 nm) with circularly polarized laser light, as also reported by several groups [240]. Figure 10.1b shows narrow nano-ripples with
~ 200 nm spacing at the peripheral regions of the laser irradiated spot with linearly polarised laser pulses. Figure 10.1c shows wider nano-ripples with about 600 nm spacing near the central hot region of the laser irradiated spot. As expected, for linearly polarized light, the nano-ripple orientation was always orthogonal to the laser polarisation [200, 201]. Nano-ripple formation was observed with 10-100 shots fired on the semiconductors. It was also observed that the number of shots fired on the semiconductor did not have any effect on the ripple period.

Figure 10.1: GaP irradiated by 800 nm ultra-short laser pulses, a) with circularly polarised beam, b) and c) linearly polarised beam in two different regions; b) is around the periphery of the irradiated spot (low fluence) and c) is in the central region (high fluence). (The length of the horizontal bar is 1μm in a, b, and 2μm in c)

Figure 10.2 shows the nano-ripple formation using linearly polarised laser pulses in normal incidence. The polarization was rotated using a half wave plate. In all the figures, the rippled grating vectors orient perpendicular to incident laser polarization. In the narrow band gap semiconductors like GaAs and InP, the SEM pictures of the irradiated spot show the spacing to be of the order of 500-600 nm. On the contrary, in wide band gap material like GaN and SiC, the
spacing is of the order of 170-270 nm. Thus, it is observed that, in general, the narrow nano-ripples are formed from material with a wide band gap. This observation of narrow ripple formation in wide band gap semiconductor is consistent with previous reported results by Borowiec et al [241], but no explanation of the physical processes involved was given in those experiments.

![Image of nano-ripple formation using 800 nm pulses in narrow band gap semiconductors: a) GaAs and b) InP; and in wide band gap semiconductors: c) GaN and d) SiC (The length of the horizontal bar is 1µm in a, b, c and d).]

Figure 10.2

Figure 10.3 shows different micro structure formations using different fluences and ambient conditions for narrow band gap semiconductors like GaAs. In all the figures, the linearly polarised laser was at normal incidence. The SEM picture of the irradiated spot, as seen in Fig.10.3a, shows that, at a high fluence in air, no nano-ripple formation takes place, and only random heterogeneities of a few microns order appear. Figure 10.3b shows the formation of nano-ripples of a typical size of 600 nm, at low fluence (in air). Interestingly, Fig.10.3c shows
formation of nano-holes at high fluence in water. Figure 10.3d shows narrow nano-ripples of 150 nm size in GaAs at low fluence in water. This shows the crucial role of the ambient medium in formation of the nano-ripples. Very narrow nano-ripples are observed in narrow band gap materials like GaAs in water, whereas in air, the corresponding nano-ripple period is of the order of the laser wavelength. Even for a wide band gap material like GaP, which shows narrow nano-ripples of period ~200 nm in air, a narrower period of 150 nm is observed during irradiation in water.

![Nano-ripple formation using 800 nm pulses in GaAs: a) at high fluence in air, b) at low fluence in air, c) at high fluence in water, d) at low fluence in water.](image)

*Fig.10.3: Nano-ripple formation using 800 nm pulses in GaAs: a) at high fluence in air, b) at low fluence in air, c) at high fluence in water, d) at low fluence in water. (The lengths of the horizontal bars correspond to 5µm in a), b) and c), and 1µm in d)*

Figure 10.4 shows the angular dependence of nano-structure size obtained from narrow (GaAs) and wide (GaP) band gap materials irradiated by 800 nm pulses in water. It was observed that for the narrow band gap (GaAs) semiconductor, the ripple size increased with increasing angle of incidence as shown in Fig. 10.4a. In the case of the wide band gap (GaP) material with increasing angle of incidence the ripple period first increase and becomes constant at higher angles, as shown in Fig.10.4b. It was mentioned earlier in the context of Fig.10.3c that, at high
fluence, nano-holes are formed in GaAs. Figure 10.4c shows that the size of the holes increases with increasing the angle of incidence of the incident p-polarised light.

*Fig10.4 : Angular dependences of formation of various nano-structures using 800 nm pulses in water :a) Nano-ripple formation in GaAs, b) Nano-ripple formation in GaP, and c) Nano-hole formation in GaAs*
In many photonic applications, for example, the two-dimensional photonic crystals and micro diffraction elements, nano / micro holes on the surface of bulk materials are required as the building blocks. Although the mechanism of formation of such structure is still not clear, this process was achieved during irradiation in water medium, thus emphasizing the role of dense surrounding medium in formation of such novel hole structures.

It is commonly accepted that the nano-ripple width is dependent on the wavelength of the incident light. Therefore, to obtain narrow nano-ripples, second harmonic of the fundamental laser radiation is a better choice. Figure 10.5 shows the influence of laser wavelength on nano-ripple formation. In all the figures the rippled grating vectors orient perpendicular to incident laser polarization, which was linear in all the cases. Figures 10.5a and 10.5b show that, in the case of SiC, the use of 400 nm wavelength reduces the ripple period by more than a factor of 2 as compared to the nano-ripples produced by the 800 nm pulses (from 190 nm to about 90 nm). Similarly, for a narrow band gap material like InP also, there is a reduction of ripple period from 620 nm to about 280 nm, as shown in Figs. 10.5c and 10.5d. It may be noted that, for GaP, the ripple period using 400 nm pulse becomes larger than that formed using 800 nm pulses (from 180 nm to about 300 nm).
Fig. 10.5: Nano-ripple formation using 800 nm pulses and 400 nm pulses respectively in wide band gap semiconductors: SiC a) and b), GaP e) and f), and in narrow band gap semiconductor InP c) and d). (The length of the horizontal bar is 2µm in a), 500 nm in b), 5µm in c), 1µm in d), 1µm in e), and 2µm in f ).

10.3 Analysis of the experimental observations

The consistent observations regarding the nano-ripple formation are: 1) the ripple period is larger at higher fluence, and 2) the ripple period is large for the materials having band gap narrower than the incident photon energy compared to that for materials having a wider band gap, 3) a denser ambient medium results in the formation of narrower ripple period. We now describe our view on the reasons responsible for the observations made in this experiment. The plausible explanation for all such observation is consistent with the theory that ripple formation is due to excitation of the surface plasmon at the semiconductor surface by the incident laser light with the rough target surface.
The surface plasmon is a well known phenomenon in the context of the metals, which have free electrons for excitation of this longitudinal charge density oscillation. However, in the case of semiconductors the origin of free electrons is because of the excitation of free electrons due to multi-photon ionization by the laser. The typical intensity of $2 \times 10^{12}$ W/cm$^2$ is just sufficient to start plasma formation for an ultra-short (45 fs) laser pulse, wherein multi-photon ionization is the dominant process [242]. These laser-generated free electrons give a transient metallic character to the molten surface, which can now support the surface plasmon [200, 201]. During the initial few shots, the surface roughness is enhanced due to irradiation by the high intensity pulses and formation of random nano-structures [243]. The subsequent shots fired on the roughened surface lead to more efficient excitation of surface plasmon [244]. The molten material assumes the shape of a grating which satisfies the relation between wave vectors of the incident laser (which depends on its wavelength, the angle of incidence and the refractive index of the ambient medium) and the surface plasmon (which depends on the electron density of the molten surface). This grating gets frozen once the material cools down as soon as the laser pulse ends giving rise to the observed nano-ripples. The wave vector of this grating satisfies the following relation, as per the momentum conservation [201]

$$G = k_i - k_s$$

(10.1)

where $k_i$ is the wave vector of incident laser, and $k_s$ is the wave vector of surface plasmon. By substituting the expression for $k$'s in terms of corresponding wavelengths, and $|G|$ as $2\pi/d$ (where $d$ is the ripple period), one gets the expression for $d$ [201] as

$$d = \frac{\lambda_L}{\lambda_L \pm \mu \sin \theta}$$

(10.2)
Here $\lambda_L, \lambda_s, \theta, \mu$ are the incident laser (vacuum) wavelength, surface plasmon wavelength, the incident angle, and the refractive index of the ambient medium. It is clear from equation 10.2 that for normal incidence (i.e. $\theta = 0$) $d = \lambda_s$. Thus, at normal incidence, the ripple period $d$ is equal to the surface plasmon wavelength, which is obtained from its dispersion relation as

$$\lambda_s = \frac{\lambda_L}{\sqrt{\varepsilon \varepsilon_m}}. \quad (10.3)$$

Here $\varepsilon$ is dielectric constant of the surface plasma created by the intense fs pulse and $\varepsilon_m$ is the dielectric constant of the ambient medium (i.e. $\varepsilon_m = \mu^2$; 1 for air and 1.76 for water). Since the multi-photon ionized surface has free electrons, its dielectric constant can be taken similar to a plasma i.e. (neglecting the collision term frequency)

$$\varepsilon = 1 - \frac{n_e}{n_c}, \quad (10.4)$$

where $n_e$ is the surface plasma free electron density and $n_c$ is the critical density corresponding to the laser wavelength. Putting the expression of $\varepsilon$ in the equation 10.3 and then using equation 10.2 one gets for the case of normal incidence

$$d = \frac{\lambda_L}{\sqrt{\varepsilon_m(1-n_e/n_c)}}. \quad (10.5)$$

From equation 10.5 it is clearly seen that the ripple period is related to the incident laser wavelength, electron density of the surface plasma, and the dielectric constant of the ambient medium. It is also evident from the expression that real values of $d$ will be obtained only if

$$n_e < n_c \quad \text{or} \quad n_e > (\varepsilon_m+1)n_c. \quad (10.6)$$

When this condition given by equation 10.6 is not satisfied, the nano-ripples are not formed.
Figure 10.6a shows the variation of nano-ripple period in air and water with electron density plotted using equation 10.5, for 800 nm wavelength. Figure 10.6b shows the corresponding curve for 400 nm wavelength.

A few conclusions can be made from these figures. There exist two branches of solutions for the nano-ripples, one is the super-wavelength nano-ripple and the other is the sub-wavelength nano-ripple. The super wavelength can be formed if the electron density is below the critical density, but such structures are not observed primarily due to two reasons, the first one is that being a low electron density process the plasmon excitation is very weak, and the second one is that the long period structure will have lower groove depth so that any short period structure may overshadow the long period one. The third possible reason could be that at such low fluence, the material simply does not melt to reorganize, thereby precluding any possibility of ripple formation. The sub-wavelength nano-ripples are formed if the electron density is greater than $n_c(e_m+I)$. The nano-ripple period is equal to laser wavelength if the electron density is high and a very sharp decrease in the ripple period is observed when the electron density starts approaching $n_c(e_m+I)$. If water is the ambient medium, then the nano-ripple period is smaller for the same electron density. Further, the figure also brings out the critical role of electron density in formation of large and narrow ripple formation. Since the electron density-generating surface during femtosecond laser pulse irradiation depends on the laser parameters like fluence and wavelength, a drastic change in the nano-ripple period is expected on a small variation of these parameters.
10.3.1 Ripple width vs. laser fluence

Now we come to the explanation of the experimental observations in terms of the above formulation. The observation from Fig.10.1 regarding narrow ripple of 200 nm width at the periphery of the focal spot and wider 600 nm ripple width in the central hot spot region can be explained as follows. Since the electron density of the laser irradiated surface is proportional to the incident laser fluence, higher intensity of irradiation in the central region of the focal spot will generate a higher electron density [245] leading to formation of wider nano-ripples of 600 nm.
spacing, whereas at the region of the edges of focal spot, a lower fluence generates a lower electron density, which leads to a narrower (~200 nm) ripple formation. It is also seen from Fig. 10.6 that a slight change in the electron density can cause a drastic change of the ripple period and this explains the observation of the large difference in the ripple period in two spatial regions. The abrupt change in the ripple period is because, as explained earlier, it is very critically dependent on the electron density (see Fig.10.6). At high intensity, ripples slightly smaller than the laser wavelength are formed, and at mid range intensity or lower intensity, the ripple period can become very narrow depending on the free electron density generated on the surface. At very low intensities, no rippling takes place, as explained earlier. Of course, the semiconductor material chosen, its band gap and material breakdown property and irradiation intensity decide the electron density generated.

10.3.2 Ripple width vs. band gap

The main observation that narrow nano-ripples are formed on wide band gap material can also be explained in a similar way. When a femtosecond laser irradiates a narrow band gap material semiconductor surface, more free electrons are likely to be available in comparison to the case if the wide band gap material is irradiated by the same laser. This is because in addition to the multi-photon excitation of electrons, the single photon absorption process will also allow the excitation of free electrons, provided the incident photon energy is larger than the band gap. Therefore, the absorption of the ultra-short pulses in narrow band gap semiconductor material is through a combination of linear and nonlinear absorption process leading to a larger availability of free electrons in the conduction band. Therefore, as observed from Fig.10.2, the ripple period is large (~600 nm) in the case of narrow band gap materials, since a higher electron density ($n_e$
leads to formation of larger width nano-ripples. On the other hand, since the generated electron density for wide band gap material is low as single photon absorption is not possible, narrow ripples are formed in this case (provided the incident laser intensity is low).

10.3.3 Ripple width in different ambient

Next, we discuss the nano-ripple formation in GaAs in air and water. The ambient medium has substantial effect on the nano-ripple formation as expected from equation 10.2. This was experimentally was observed by Ganeev et al [246] for methanol as the surrounding medium. Our experiments in air and water were carried out at two fluences. At higher fluence, no nano-ripple formation takes place. As seen in Fig.10.3a, only random heterogeneities of few microns order (~ 2.5 μm) appear. At low fluence, sub-wavelength nano-ripples of 600 nm period are formed (Fig.10.3b). Such micron order microstructures have also been observed by Huang et al. [247]. They observed that as the laser fluence increases, the ripples become disordered due to the enhancement of the thermal effects. Also, as the laser fluence becomes high, the surface morphology evolves and the degree of ripple irregularity becomes large resulting in the dominant shift of spatial scales of the laser-induced structures from a few hundred nano-meters to a few micrometers. Next, in water, a drastic reduction of the nano-ripple period is recorded from 600 nm in air to about 150 nm in water. Such a reduction in nano-ripple period is expected from Fig.10.6 as already discussed. An interesting observation is that at high fluence irradiation of GaAs in water leads to nano-hole formation. The reason of nano-hole formation is still not understood, although its seems to be like a self organization process due to surface tension relaxation of strained molten GaAs against another liquid (in this case, water). The experiment
was repeated at low fluence for GaP (wide bandwidth material) which shows 200 nm nano-ripple period in air and 150 nm in water.

### 10.3.4 Ripple width at different incident laser angle

Many groups have done nano-ripple width study with different incident angles of the laser [248, 249]. There are contradictory observations regarding this, as some have reported increase of period with increase in angle of incidence [248], whereas some have shown decrease in the ripple period with angle of incidence [249]. In our experiment, we recorded an overall increase in ripple period with the angle of incidence for GaAs in water. As shown in Fig.10.4 a. GaP in water also shows an increase of ripple period from 150 nm to 300 nm, as the angle is increased from normal incidence to an angle of 30°. However, the ripple period saturates at larger angles as seen from Fig.10.4b. These trends can be partially explained from equation 10.2 if one takes the "minus" sign. In that case, the denominator decreases in magnitude as the angle of incidence in increased, leading to an increase in the ripple period. Although this explanation holds true for GaAs which shows a continuous increase of ripple period with increasing angle, the same is not correct for GaP where ripple period shows saturation at larger angles. This shows that it is important to consider other factors which contribute to the variation of ripple period with angle of incidence. The most crucial among them is perhaps the electron density of the surface plasma created after irradiation of the semiconductor. The electron density generated, in turn, depends on the laser irradiation conditions (fluence, laser wavelength etc.) [245], material properties (band gap, melting point etc.) [20], and the absorption of laser energy in the material through linear (single photon absorption) and non linear processes (multi-photon absorption). As the angle of incidence is increased, the circular focal spot gets elongated and becomes elliptical, leading to a decrease in
the laser fluence. For example, at an incident angle of 45°, the fluence becomes about 70% of the fluence at normal incidence. Therefore, as the angle is increased, the fluence decreases, resulting in the decrease of electron density of the surface plasma. This should lead to a decrease in the ripple period. However, as the angle of incidence is increased, the laser energy absorption also increases (up to the Brewster angle). The increase in the absorption is because the reflectivity of the p-polarized light keeps decreasing as the angle of incidence increases and approaches the Brewster angle. The range of angles covered by us is below the Brewster angle of the semiconductor (the Brewster angle of semiconductors is as high as 70-80°). This decreasing reflectivity leads to an enhanced absorption and hence a higher electron density, which should result in generation of larger period ripple. Therefore, resultant ripple period is governed by the above two competing processes of electron generation, one being fluence and the other being absorption. On increasing the angle of incidence, the fluence reduces and less electron generation is expected, but on the other hand, on increasing the angle, more laser light absorption will occur resulting in more electron generation. The relative dominance of the electron generation process viz. laser energy absorption or laser fluence, determines whether as a function of angle the electron density decrease or increase. One can now explain the observation that in the case of GaP the ripple period initially increases and then becomes nearly constant at larger angles (Fig.10.4b). It seems that in our experimental conditions, the laser energy absorption and the laser fluence compete against each other equally. The generated electron density is such that the ripple period becomes constant at higher angles for GaP. The monotonic increase of ripple period with the angle of incidence in the case of GaAs (Fig.10.4a) implies that the electron density in this case is continuously increasing on increasing the angle. This means that electron generation is dominated by absorption process and the fluence has comparatively less influence in the case of
GaAs. Had fluence been the more important parameter, the electron density would be reduced on increasing angle (due to the decrease of fluence), and the nano-ripple period would have decreased. Further, it may be noted that for s-polarized light, the period should be independent of the angle of incidence as the magnitude of the laser $k$ vector in the direction of the surface plasmon remains unchanged in this case. However, as the angle increases, due to increasing reflectivity (due to s-polarization), the absorption of the laser light will keep decreasing with angle, leading to lower electron density and corresponding decrease in ripple period. Interestingly, the nano-holes formed on GaAs (at high laser fluence, in water) also showed increase for the hole diameter for higher angles of incidence (Fig.10.4c). Further experiments are needed to understand their generation mechanism.

10.3.5 Ripple width vs. incident wavelength

The role of the laser wavelength in changing the ripple period is seen from Fig.10.5. As expected from equation 10.5, the ripple period is expected to decrease by a factor of 2 as one goes from fundamental to the second harmonic laser beam, with other conditions remaining the same. This is precisely what is seen in Fig.10.5a for SiC (a wide band gap (3.37 eV) material for both wavelengths) and Fig.10.5b for InP (a narrow band gap (1.35 eV) material for both wavelengths). In both the cases, there is a reduction in the ripple period by a factor of 2 (190 nm to 90 nm and 620 nm to 280 nm). The observation in the case of GaP is just the opposite. Here the ripple period is observed to double (180 nm to 300 nm) instead of becoming half. This is because, GaP has a band gap energy of 2.3 eV, which is wide for 800 nm radiation (~ 1.56 eV), but narrow for 400 nm radiation (~3.12 eV). So, as a wide band gap material, GaP shows a
narrow ripple period (180 nm) for the fundamental (800 nm) and as a narrow band gap material, it shows larger ripple period (300 nm) for the second harmonic radiation (400 nm).

Fig.10.7 : Observed nano-ripple period as a function band gap. The dotted line indicates the incident laser photon energy for a) 800 nm pulses, and b) 400 nm pulses

The above correlation of the band gap with ripple period becomes more obvious in Fig.10.7. The vertical dotted line in Fig.10.7a is the photon energy of the 800 nm laser and for Fig. 10.7b the dotted line represents the photon energy of the 400 nm laser radiation. From these two graphs, it is clear that if the band gap of the semiconductor material is narrower than the incident photon energy, the ripple width formed is slightly less than, but of the order of the laser wavelength. For
the materials having a band gap larger than the energy of the laser photon, the ripple period is much smaller (typically of the order of 1/4th laser wavelength). The reasons for this difference have been already explained earlier in terms of single photon and multiple photon ionization of the molten surface.

10.3.6 Nano-ripples and melting point

Although most of the observations of ripple formation could be explained from the above formulation, there could be other parameters, which are responsible for finer variations of different nano-ripple formation of different materials. We have neglected the material parameters like melting point, conductivity of semiconductors, charge mobility, surface tension and viscosity of the molten material of the surface, which may also be very critical in deciding the resultant structure. For example, melting is one of the primary requirements of restructuring the surface.

To see if the melting point plays a deciding role in ripple period, the ripple period has been plotted in Fig.10.8 as a function of melting point for various materials, at a constant laser fluence.

![Graph showing the relationship between melting point and ripple period for various semiconductors.](image)

*Fig.10.8: Observed nano-ripple period as a function of melting point for various semiconductors*
There is clear trend which shows materials having a high melting point form narrow ripples. Fig.10.8 seen in isolation would give an impression that melting point decided the ripple period. However, when seen with Fig.10.7b for the ripples formed with second harmonic laser beam, it becomes clear that looking at GaP ripple period, it is the band gap (relative to the laser photon energy), which decided the ripple period, and not the melting point, although melting is crucial in nano-ripple formation.

The observations which still need explanation are: 1) formation of nano-islands with circularly polarized light (Fig.10.1a); and 2) formation of nano-holes at high fluence irradiation under water (Fig.10.3 c).

The above studies have shown that, in general, narrow nano-ripples are formed from materials with a wide band gap. The width of the nano-ripples also decreases with the laser wavelength and the laser fluence. Under specific conditions, nano-hole formation is observed over a large area. The ambient medium can further help in narrowing down the ripple period formation. The observations are explained by considering the photo-ionization of the molten semiconductor surface on irradiation with intense femtosecond pulses, which support surface plasmon excitation, which in turn interferes with incident laser light to give rise to the ripple formation. The nano-ripples get frozen due to fast cooling once the laser pulse is over.

It must also be mentioned here that recent experiments have shown grating targets when irradiated with intense laser pulses leads to enhanced absorption, x-ray emission and high energy collimated electrons generation [162, 169, 195, 250]. Nano-ripples resemble grating like surface structure which may also be produced by ultra-short laser pulses on interaction with a solid surface. Properties of nano-ripples depend primarily on the ripple width. One can exploit the surface plasmon excitation in nano-ripples and the electron density at which this excitation will
take place. The surface plasmon excitation can be achieved at solid density from nano-ripples of ripple width of the order of wavelength. Therefore nano-ripples can be another candidate of in situ formed nano-structured targets and this possibility has to be explored in future.