Origin of Periodic Modulations in the Transient Reflectivity Signal at Cryogenic Temperatures

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Periodic modulations that appear in the low-temperature transient reflectivity signal of a GaAsP/AlGaAs single quantum well is studied. Similar anomalous oscillations are also observed in layered manganite [K. Kouyama et al. J. Phys. Soc. Jpn. 76:123702(1–3), 2007]. We show that such periodic modulations are caused by changes in the linear reflectivity of the sample during transient reflectivity measurements. Studied carried out on reflectivity of different materials under identical conditions shows that these modulations on the true transient reflectivity signal are caused by condensation of residual gases on the surface of quantum well. Methods to obtain reliable transient reflectivity data are also described.

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I. INTRODUCTION

Femtosecond pump-probe spectroscopy is used for studying the sub-picosecond carrier response of materials which are to be used in devices like lasers, modulators, detectors etc. For nanostructured materials grown on opaque substrate in optoelectronic devices,
very often it becomes necessary to do the pump-probe measurements in a reflective geometry \[4-6\]. In such measurements the transient change in reflectivity, \( \Delta R/R \) can be as low as \( \sim 10^{-6} \). Similar to transient reflectivity several other well known techniques like photomodulated reflectivity and ellipsometry also use reflection geometry \[4-8\]. Hence to get reliable data from these techniques it is essential to maintain the quality and purity of the sample surface. In order to achieve this good surface quality cleaving or etching of the surface is done just before the experiment or in-situ measurements are carried out.

In the pump-probe technique, transient reflectivity measurement of a sample can take few tens of minutes for a complete a scan. Thus, even a slow surface contamination process can modulate the actual signal originating from the ultrafast response of the sample. Transient reflectivity measurements carried out at low temperatures on \( La_{0.5}Sr_{1.5}MnO \) showed oscillations in the signal with an anomalously long time period which is not well understood \[9\]. Similar periodic modulations were also reported in reflectivity measurements on bulk ZnO \[10\]. Our transient reflectivity measurements on GaAsP/AlGaAs quantum wells at low temperatures showed similar modulations in the transient reflectivity signal. By studying reflectivity of different materials under similar experimental conditions as that of quantum wells we show that these modulations on the actual transient reflectivity signal are caused by condensation of residual gases on the surface of quantum well. We also show the various precautionary measures which can be taken to obtain reliable transient reflectivity data.

II. EXPERIMENT

The transient reflectivity measurements were carried out in a standard degenerate pump-probe geometry with a 90 fs, 82 MHz Ti:Saphire laser \[5,6\]. The laser was operated at peak wavelength of 786 nm during transient reflectivity measurements. The samples under study were mounted in a closed-cycle cryostat, which was evacuated by a diffusion pump connected through a liquid nitrogen trap \[11\]. The sample temperature was kept stable within 0.1 K during the experiments. The residual pressure inside the cryostat was of the order of \( \sim 10^{-6} \) millibar. The pump and probe beams were made to fall on the sample kept inside the cryostat through an one inch optical window. The angle of incidence of pump and probe beams on the sample were \( \sim 0^\circ \) and \( 10^\circ \) respectively. The pump beam was mechanically chopped and the reflected power of the probe beam from the sample was detected by a photodiode
and lock-in-amplifier combination. The change in reflectivity of probe pulse caused by the pump pulse was then recorded at different pump-probe delays. The complete evolution of the transient reflectivity during the first few hundreds of picosecond after excitation by the pump pulse was built up by taking such repeated observations at different pump-probe delays. This process of data accumulation takes a few tens of minutes to complete. The samples used in our transient reflectivity studies was a GaAsP/AlGaAs single quantum well (QW). Quantum well structure was formed by growing a GaAs_{0.86}P_{0.14}/Al_{0.7}Ga_{0.3}As in between Al_{0.7}Ga_{0.3}As barriers of thicknesses 250 nm and 50 nm thickness on the bottom and top sides. The QW structure is deposited on a [001] n+ doped GaAs substrate [12].

III. RESULTS AND DISCUSSION

Figure 1 shows the transient reflectivity signal from GaAsP/AlGaAs quantum well measured at room temperature (300 K). The 786 nm wavelength of the laser excites photocarriers in the quantum well as well as the GaAs substrate. These photo-excited carriers modifies the refractive index, and hence the reflectivity of the quantum well structure. This results in the fast initial rise with time constant nearly 6 ps. This initial fast change in the reflectivity recovers in \( \sim 630 \) ps due to the relaxation and transport of the carriers. Repeated measurements under identical sample conditions shows that the transient reflectivity signal remains same within the experimental errors (Fig. 1). However, the low temperature transient reflectivity shows a very different behavior. Figure 2 shows the transient reflectivity of the same sample measured at the same experimental conditions but at 50 K. Finer analysis of the data shows that the low temperature transient reflectivity signal was similar in nature as that of room temperature but with additional oscillatory modulations on it. Transient reflectivity measurements on \( \text{La}_{0.5}\text{Sr}_{1.5}\text{MnO} \) at low temperatures showed oscillations in the signal similar to that reported here [9]. However, they have reported that the origin of these oscillations in the transient reflectivity signal is not clear yet. Repeated measurement of transient reflectivity of the QW sample shows that the phase of the oscillations in the signal kept changing on each scan. This causes the transient reflectivity profile to change markedly in each scan (Fig. 2). In fact we find that when the temperature of the sample was below 200 K the transient reflectivity signal becomes not repeatable. The linear reflectivity of the QW sample measured by using the probe pulse and by blocking the pump beam, itself showed
such periodic oscillations. Due to such oscillations, if the linear reflectivity measurement starts at an arbitrary time the initial phase of the oscillation is different. These modulations in the linear reflectivity of the sample causes the transient reflectivity signal to change at each scan.

In order to understand the variations in the linear reflectivity of the samples and to avoid high intensity effects we have performed the same linear reflectivity measurement at 632.8 nm using a continuous wave low-power He-Ne laser. Figure 3 shows the variations measured in the linear reflectivity of the QW sample at 50 K. The measured linear reflectivity of the sample clearly shows an oscillatory behavior which was not noticeable at sample temperatures above 200 K. These periodic modulations on the signal was similar in nature to that reported for bulk ZnO [10]. These oscillations in the linear reflectivity in their case has been attributed to space change effect. To identify the cause for the observed changes in the linear reflectivity our QW sample, a material dependence study has been carried out on various samples, a glass plate (insulator), a bulk GaAs wafer (semiconductor) and a bulk Aluminium block (metal). The surface of these bulk materials were of optical quality. The variations in the linear reflectivity of these samples are also shown in Fig.3. The oscillations in the linear reflectivity of GaAs wafer remained nearly same in frequency and magnitude as that of the QW sample. The magnitude of oscillation was found to be largest for glass. The observation of similar periodic variations in the linear reflectivity of different kinds of materials implies that the oscillations has a common origin independent of materials. We attribute the observed oscillations in the reflectivity of the sample to condensation of water vapor, residual gases and organic impurities present in the vacuum chamber on the surface of the sample at low temperatures. As the sample cools, a thin film of condensate starts growing on its surface. The resulting interference between the reflection from the top and bottom interfaces of the growing film can give rise to the observed modulations in the measured linear reflectivity oscillations. This would also explain why similar oscillations are observed in all the materials under study.

In order to estimate the growth rate and the refractive index of the condensate material we model the effect of a continuously growing thin film on the reflectivity of the sample. Let \( l \) be the thickness of the thin film growing on the sample at time \( t \). The net reflectivity of
the film and the sample top surface at any given time is

\[ R = \frac{R_1 + \Omega R_2 + 2\Omega \sqrt{R_1 R_2} \cos \left( \frac{4\pi n' l}{\lambda} \right)}{1 + \Omega^2 R_1 R_2 + 2\Omega \sqrt{R_1 R_2} \cos \left( \frac{4\pi n' l}{\lambda} \right)}, \]  

where \( R_1 \) is the reflectivity of the air and thin film interface and \( R_2 \) is the reflectivity of the thin film and sample interface. \( n' \) and \( n \) are the refractive index of the thin film and sample materials at the wavelength of the light used. The absorption loss per pass \( \Omega \) is \( \exp(-\alpha l) \), where \( \alpha \) is the linear absorption coefficient of the thin film material. Figure 5 shows the calculated reflectivity oscillations using Eq.1 for 632.8 nm wavelength for different values of \( n' \), \( g \) and \( \alpha \). For a given growth rate and \( n' \) of a non-absorbing thin film, the period as well as the magnitude of oscillations remains constant with time. This can be explained as follows: if either the sample or the film is a poor reflector, then \( R_1 R_2 \ll 1 \) and the denominator can be taken to be nearly 1 with this approximation and assuming that the film thickness increases linearly with time the above equation written as

\[ R(t) = A + B \cos \left( \frac{4\pi n' g t}{\lambda} \right), \]  

where \( g = dl/dt \) is the growth rate of the film and \( A = R_1 + R_2 \) and \( B = 2\sqrt{R_1 R_2} \). Thus, a non-absorbing thin film with constant growth rate and \( n' \) will have constant amplitude as well as constant time period. Assuming that the growing thin film on our samples to have constant growth rate, constant refractive index and no absorption, we fit the experimental data using Eq.1 to have an estimate for the refractive index and growth rate of the film. Figure 6 shows linear reflectivity of measured from the GaAs along with its best fit using Eq.1. Table I shows the estimated refractive index and growth rate of the thin films condensing on different samples derived from these fittings. In case of cryo-vacuum condensation of gases, the crystalline structure, and density of the condensed film depends on temperature, ambient atmosphere. The material and surface quality of the sample on which the gases are condensing will also effect the growth rate and refractive index of the thin film. Thus, the estimated refractive index and growth rates of the films are expected to vary with the underlying sample.

Figure 7 shows the measured time dependence of linear reflectivity measured from the glass surface over a long observation period. Although the variations in the period of oscillations and the magnitude can be neglected over one cycle, the long time observation clearly shows an increase in the time period as well as changes in the magnitude of oscillations.
Similar changes in the period of oscillations as well as the magnitude has been found for all the samples. In Fig. 5 we have also shown the simulated changes in the reflectivity of the sample-thin film structure for the two cases: first the film has finite absorption and and second the growth rate decreases linearly with time. The observed changes in the magnitude and period of oscillations in the linear reflectivity of the sample shown in Fig. 7 can be explained if we assume the thin film to have finite absorption and reduction in growth rate as it grows. It is expected that as the condensation starts, the amount of residual gas present in the chamber reduces and this can lead to reduction in the growth rate of the film. Thus, the observed oscillatory behavior in the linear reflectivity is consistent with our model of condensation of a thin film on the samples surface. In such thin film formation the growth rate should depend strongly on the temperature of the sample. It is expected that as the temperature of the sample increases the growth rate should reduce and hence the period of oscillations should increase. Figure 5 shows the temperature dependence of period of oscillations on the reflectivity of GaAs sample. Clearly the time period of reflectivity oscillations increases with increase in temperature, supporting the formation of thin film on the material under study.

Having understood the cause of modulations in the linear reflectivity, it is essential to suppress these oscillations to get the proper transient reflectivity signal. In order to reduce the amount of residual gases, the cryostat was conditioned by purging with nitrogen and baking under vacuum. The reflectivity under various stages of conditioning is shown in Fig. 9. Purging with nitrogen removes some of the residues this results in increase of the time period of oscillation in the reflectivity. However with a vacuum level of $1 \times 10^{-6}$ millibar, some amount of condensation is still observed. What helps the most in reducing condensation, as shown in Fig. 9, is the mounting of a metal shield around the sample with through holes for optical beams. This is because, a large fraction of the residual gases condense on the shield and do not reach the sample inside. Figure 10 shows two representative scans of the transient reflectivity curve of the QW sample at 50 K after the cryostat is conditioned and with the metal shield in place. It is clear that with the slow oscillations in linear reflectivity suppressed, the transient reflectivity signal becomes repeatable and reliable.
IV. CONCLUSION

We have shown that the periodic oscillations observed in transient reflectivity signal measured by the pump-probe technique is caused by a film slowly condensing on its surface. In transient reflectivity measurements based on pump-probe technique, the evolution of the reflectivity is built up by taking repeated observations at different pump-probe delays and therefore the full measurement can take tens of minutes to complete. Thus even a film with a growth rate as slow as a few nm/min can cause modulations in the measured ultrafast transient reflectivity signal. We believe that the reflectivity oscillations observed in earlier reports could be due to this film growth phenomenon [9, 10]. Our studies on different samples at various temperatures and the reduction in growth rate with time shows that the source of the film formation is due to the residual gases inside the chamber. The measures required for proper conditioning of cryostat for low-temperature transient spectroscopy experiments are also presented. We also believe that maintaining a vacuum level better than $1 \times 10^{-6}$ millibar inside the chamber will reduce the amount of residual gases and will improve the reliability of the measured transient reflectivity signal. Since the process of film growth is independent of materials, the reported precautions are important for reflection based experiments with any sample.

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FIG. 1: Two representative scans of transient reflectivity signal from GaAsP/AlGaAs quantum well at room temperature (300 K) under identical conditions. The data was always repeatable within the experimental errors.
FIG. 2: Two representative scans of transient reflectivity signal ($\Delta R/R$) of GaAsP/AlGaAs quantum well at 50 K. The time evolution of the signal was different on each scans.
FIG. 3: The variations in the linear reflectivity of various materials at 50 K (wavelength of laser 632.8 nm). For ease of viewing, the reflected signal has been normalized by dividing it with its corresponding mean value.
FIG. 4: Schematic of multiple reflection from a thin film-substate system. $l$ is the thickness of thin film. $n'$ and $n$ are the refractive index of the thin film material and the sample respectively.
FIG. 5: The calculated variation of linear reflectivity from a sample and a thin film on its top surface with time using Eq.\ref{eq:1} thick line - constant $g$ and no absorption in the film ($\alpha = 0$), thin line - constant $g$ with finite absorption in the film and dashed line - linearly decreasing $g$ and $\alpha = 0$. 
FIG. 6: The variation of the measured linear reflectivity of bulk GaAs sample. The calculated curve is the best fit with Eq. 1 neglecting any absorption in the film. For ease of viewing, the reflected signal has been normalized by dividing it with its corresponding mean value. The refractive index of the GaAs used in fitting as well as the best fit parameters are given in Table 1.
FIG. 7: Measured time dependence of the linear reflectivity of a glass plate in an optical cryostat at temperature 50 K in much longer time of observations. For ease of viewing, the reflected signal has been normalized by dividing it with its corresponding mean value.
FIG. 8: The temperature dependence of period of linear reflectivity oscillations measured from bulk GaAs.
FIG. 9: Reflectivity signal for glass at 50 K under different nitrogen purging times as well as with an additional metal shielding around the sample.
FIG. 10: Two representative scans of transient reflectivity of GaAsP/AlGaAs quantum well at 50 K after conditioning the cryostat and with the metal shield a around the sample.
TABLE I: The estimated values of refractive index $n'$ and growth rate of the film condensing on different materials. The refractive index of the material used in the calculations are also given. The wavelength is 632.8 nm.

| Material | $n$  | $n'$ | $g$ (nm/minutes) |
|----------|------|------|------------------|
| Aluminium | 0.04 | 1.38 | 2.5              |
| Glass    | 1.54 | 1.34 | 8                |
| GaAs     | 3.3  | 1.15 | 7                |