CHAPTER-6

SUMMARY AND CONCLUSIONS
CHAPTER – 6
SUMMARY AND CONCLUSIONS

The experimental exploration of the quantum confinement and residual stress effect have been described and discussed at length separately for V$_2$O$_5$, Nb$_2$O$_5$ and Ta$_2$O$_5$ in earlier chapters 3, 4 and 5 respectively. We will summarize the experimental results for all the three oxides by comparing them along with the conclusions in this chapter. However, we have studied the quantum confinement and residual stress effect in crystalline phase of Nb$_2$O$_5$ and Ta$_2$O$_5$ and amorphous phase of V$_2$O$_5$. The interesting outcome of the study of residual stress is the manifestation of crystalline to amorphous phase transformation driven by the residual stress in Nb$_2$O$_5$ and Ta$_2$O$_5$ due to their extremely large elastic constants. In contrast, as grown V$_2$O$_5$ films remain amorphous for the entire range of film thickness used to study the two effects. Although, quantum confinement can be compared in these three oxides irrespective of their phases, the residual stress effect is hard to compare in crystalline and amorphous phases as stress cannot be defined directly or properly in amorphous phase.

Now, some of the aspects of this study of these three oxides will be summarized in the form of comparison irrespective of their phases, viz, crystalline of amorphous. First of all, the choice of constant flux rate for the growth of dots of the three oxides follow a linear relation with their corresponding molecular weight as shown in figure 6.1. Experimentally, the flux rate for the three oxides was optimized purely with the intention of size control depending on their growth trend. The trend of directly proportional flux rate to the respective molecular weight exhibited by the three oxides in figure 6.1 is probably the manifestation of nucleation and growth process requiring an appropriate amount of matter for the controlled growth of the respective material. Although it is not surprising, it is not trivial or obvious too. More interestingly, the chosen flux rates for the three materials scale with their melting points as shown in the inset of figure 6.1. However, this is not very surprising because the flux rate will be directly proportional to the temperature of the material above its melting point. The control and maintaining the temperature above the melting point will become difficult with increasing melting temperature as depicted in the inset of figure 6.1. Therefore,
the chosen flux rates follow a linear dependence on the respective melting point of the material as consistent in this study.

**Figure 6.1** Dependence of Flux rate used for the growth on the molecular weight for the three oxides. The inset shows the scaling of flux rates with the melting point for the three oxides.

We will further analyze the growth of quantum dots of the three oxides by plotting growth time as function of constant flux rate for few small dot sizes as illustrated in figure 6.2. As the growth flux rates were linear with respect to both molecular weight and melting point, the growth time for growing the same dot size could be expected to be linear with flux rates for the three oxides. However, it does not seem so as can be seen from figure 6.2. The dependence of growth time on flux rates for a constant dot size varies with dot size. The down word curvature changes to upward and grows with dot size implying a complex nucleation and growth process differently in these three oxides. Therefore, we have tried to fit the experimental data to some mathematical
form for a possible better understanding of the growth process. The curves representing the second order polynomial of exact form shown in the figure fit perfectly the experimental data in the figure. There could be specific growth process indicated by these which we could not analyze further due to the lack of few material specific information required for the various nucleation and growth theories. We will pursue this interesting fact later.

![Figure 6.2](image)

**Figure 6.2** Relation between the growth time and constant flux rate for the growth of few dot sizes indicated in the figure for the three oxides. The various curves represent the second order polynomial (shown with each curve) fitted to the experimental data.

The main observation is that very small dot sizes grow faster in case of Nb$_2$O$_5$ as compared to other two oxides considering their flux rates as indicated by the downward curvature seen for the growth of 2 nm dot in the figure. However this trend changes with the dot size and it becomes the slowest with the growing dot size as indicated by the increasing upward curvature. The growth trends of other two oxides
Chapter 6: Summary and Conclusions

seem to be nearly linear. It clearly indicates different nucleation and growth processes in the three oxides. More deeper and quantitative analysis will probably help to understand the observed growth of these dots which would be too ambitious in the present study. Therefore, even if it is quite interesting and desirable, it can be addressed separately later.

Figure 6.3 The evolution of dot size with time for the three oxides. The curves are the best fit to the experimental data. The corresponding equations of best fit are also shown in the figure.

In an another perspective the growth of dots can be examined by plotting the dot size as the function of growth time for the more practical point of view and applications. This is what has been displayed in figure 6.3. The evolution of dot size with time for the three oxides seems to differ quite a bit at the outset. The figure indicates yet another perspective of growth of the dots. Although, the best fit follows a second order polynomial, the extremely small second order coefficients indicate the growth of all three oxides dots follow a nearly linear dependence on time which is of great importance from the applications point of view. Further, if we fit the experimental data to a linear trend, we can easily infer that the dot growth is fastest for V$_2$O$_5$ and
slowest for Nb₂O₅ as evident from their decreasing slopes. It implies that the dot growth is not simply directly proportional to the flux rate; rather it would depend on the nucleation and growth process operative for the particular material. Therefore, for all the practical purposes, the three oxides can be considered as having a linear dependence of dot size growth with time. This fact must be useful for any practical applications of these dots.

Now, we will compare and analyze the quantum confinement in these dots of the three oxides. The first thing is to plot the observed experimental parameters $\Delta E_g = E_g(QD) - E_g(bulk)$ against the dot size as has been illustrated in Figure 6.4.

**Figure 6.4** Observed increase in energy gap $\Delta E_g$ due to quantum confinement effect with dot size for the three oxides. Each curve represents the best fit of the data and the equation of the best fit is also shown with the corresponding curve.
The experimental data can be fitted well with the equations shown with the respective oxide in the figure 6.4. As discussed in earlier chapters, the known quantum confinement effect with dot size in crystalline materials can best be expressed by the equation shown in the figure 6.4. However, in the absence of exact formulation of quantum confinement in amorphous dots, same equation can be used for analyses although the effective mass approximation is strictly not valid. Comparing the fitted equations of the three oxides with that shown in the figure 6.4, we can see that the $1/d^2$ dependence is not exact, but the power of $d$ lies between -0.86 and -1.92 as can be seen in the figure 6.4. Surprisingly, the nature of quantum confinement in amorphous $V_2O_5$ is very close to that of crystalline phase in contrast with the more deviating nature of crystalline $Nb_2O_5$ and $Ta_2O_5$ dots. The similar quantum confinement nature in crystalline and amorphous phases of $V_2O_5$ could possibly due to the similar short range structural units in the two phases. However, a large deviation of quantum confinement nature from ideal behavior even in crystalline $Nb_2O_5$ and $Ta_2O_5$ dots is a big surprise which causes curiosity in further exploration and understanding the phenomenon in such materials. As the slopes of these fitted equations can be used to determine the excitonic effective mass $\mu$ (or simply $m^*$) for the purpose of comparison with that of the crystalline phase, there is no such data available in the literature for $Nb_2O_5$ and $Ta_2O_5$. We continue to explore the nature of confinement in these oxides further more explicitly by comparing the $\Delta E_g$ versus $1/d^2$ plot for amorphous $V_2O_5$ and crystalline $Nb_2O_5$ and $Ta_2O_5$ phases as shown in figure 6.5.
Figure 6.5 $\Delta E_g$ versus $1/d^2$ plot for amorphous V$_2$O$_5$ and crystalline Nb$_2$O$_5$ and Ta$_2$O$_5$ dots. The various symbols represent experimental data and the lines represent the best fit (the numerical equation shown for each oxide in the figure).

The various lines in the figure 6.5 represent the best linear fit to the experimental data (indicated by the numerical equation for each oxide in the figure 6.5) according to the equation shown in the figure depicting the change in band gap due to dot size in quantum confinement regime. The different symbols represent the experimental data as identified in the figure 6.5 for the three oxides. It may be noted that the linear fit was done by setting the intercept as zero in consistence with the confinement equation shown in the figure. As can be seen from the equation, the excitonic effective mass $\mu$ is inversely proportional to the slopes indicating an increasing $\mu$ from V$_2$O$_5$ to Ta$_2$O$_5$ and to Nb$_2$O$_5$. The $\mu$ determined for V$_2$O$_5$ tallies well with that reported in the literature as mentioned in chapter 3 in consistence with the predicted confinement effect even in amorphous phase as explained above. However, the $\mu$ determined for
Ta$_2$O$_5$ and Nb$_2$O$_5$ may not be very accurate due to their deviated confinement behavior from that predicted as explained above. Still, they will serve as useful indicative values for the two oxides in the absence of data in the literature.

The quantum confinement mainly depends on two parameters, the dot size $d$ and the excitonic effective mass of the oxide. So far we have analyzed in detail the effect of $d$ in three oxides as discussed above. We can rewrite the confinement equation as shown in figure 6.6 and plot $\Delta E_g$ against $1/m^*$ (or $1/\mu$) for comparison of the three oxides as has been done in the figure.

![Figure 6.6](image)

**Figure 6.6** $\Delta E_g$ as the function of $1/m^*$ (or $1/\mu$) for different dot sizes of the three oxides.

This is yet another perspective of quantum confinement depicting the role of $\mu$ for the three oxides. This figure is also consistent with the analyses and discussions drawn by figures 6.4 and 6.5, however, depicting the role of effective mass explicitly on the
quantum confinement. Importantly, the role of $\mu$ seems to be pronounced for small dots due to larger $\Delta E_g$. Both Nb$_2$O$_5$ and Ta$_2$O$_5$ show deviations from the general trend shown for 1.5 nm dot. Therefore, the $\mu$ determined from this study for Nb$_2$O$_5$ seems to be smaller and similarly for Ta$_2$O$_5$ larger as evident from the figure 6.6. However, still the values of $\mu$ determined here for the three oxides seem to be consistent as evidenced by the linear relation between $\mu$ and $\Delta E_g$ observed in the figure for any dot size. Therefore, we can conclude that the study of quantum confinement in the three oxides is quite consistent with various confinement parameters as analyzed by different perspectives explained above.

It would be difficult to summarize the residual stress effect in the three oxides in the form of comparison due to the fact that one is amorphous (V$_2$O$_5$) and other two are crystalline (Nb$_2$O$_5$ and Ta$_2$O$_5$). The residual stress effect in amorphous phase of V$_2$O$_5$ has been manifested through the changing bond lengths of various pairs of atoms of short range structure in an indirect way. In contrast, the residual stress effect is directly manifested through the changing d-spacing of the most intense diffraction peak as observed for Nb$_2$O$_5$ and Ta$_2$O$_5$. Out of these three oxides, only V$_2$O$_5$ behaves differently, while Nb$_2$O$_5$ and Ta$_2$O$_5$ have similar behavior with similar related parameters. The residual stress induced amor phization has been demonstrated in this study for the first time for Nb$_2$O$_5$ and Ta$_2$O$_5$ in consistency with the limited reports of pressure induced amorphization in these two oxides. The study of residual stress effect in these two oxides in crystalline forms shows similar magnitude of pressure coefficients of optical band gap for the two oxides.

**Conclusions**

- The quantum dots of V$_2$O$_5$, Nb$_2$O$_5$ and Ta$_2$O$_5$ have been grown by a fairly simple and most common method of physical vapor deposition (vacuum thermal evaporation) utilizing the early stage of nucleation and growth stage. This method facilitates an easy way of dot size control through growth time and the growth of very small dots ($\approx 1.5$ nm) have been possible. The dot size
distributions were close to mono-disperse-like for small dots which is advantageous for practical applications.

- The EDAX and electron diffraction of the dots reveal that all the dots of V$_2$O$_5$, Nb$_2$O$_5$ and Ta$_2$O$_5$ grown by this method on glass substrate at room temperature are stoichiometric, amorphous (V$_2$O$_5$) and crystalline (Nb$_2$O$_5$ and Ta$_2$O$_5$) without any exception.

- The nearly linear relationship of dot size (for all three oxides) with growth time at low flux rate facilitates the growth of desired dot size and fine tuning of dot sizes. The choice of flux rate can serve an additional parameter for the growth process and size selection.

- The Raman and IR analyses of the dots indicate that the crystalline structure and stoichiometry of dots are the same as that of the starting material for Nb$_2$O$_5$ and Ta$_2$O$_5$.

- The magnitude of blue shift of optical energy gap due to quantum confinement of the three oxides scales with dot size as predicted by the theory irrespective of whether they are crystalline or amorphous.

- This study shows that the nature of quantum confinement in V$_2$O$_5$ dots is almost similar in amorphous and crystalline phases while they deviate slightly even in case of crystalline dots of Nb$_2$O$_5$ and Ta$_2$O$_5$.

- The residual stress effect in amorphous phase of V$_2$O$_5$ has been manifested through the changing bond lengths of various pairs of atoms of short range structure in an indirect way while it is directly manifested through the changing d-spacing in crystalline Nb$_2$O$_5$ and Ta$_2$O$_5$.

- Both pressure coefficient of band gap and crystalline to amorphous transition for tetragonal Nb$_2$O$_5$ and orthorhombic Ta$_2$O$_5$ via residual stress have been determined in thicker films for the first time in the literature.

- Both Nb$_2$O$_5$ and Ta$_2$O$_5$ show similar magnitude of pressure coefficient of Band gap and crystalline to amorphous transition at comparable pressures consistent with the literature.
Scope for future work

This study demonstrated the possible growth of quantum dots of technologically important some group V oxides using a simple growth technique. In the process, it was found that it really does not matter much whether the resulting dots are amorphous or crystalline as far as the confinement effect is concerned. This opens up the motivation, scope and interest in exploring various aspects such as the short range structural similarity in amorphous and crystalline dots, nature of quantum confinement in amorphous phase, the effective mass concept in amorphous phase at nanoscales, emissive properties (like photoluminescence) of amorphous dots and the other relevant phenomena concerning quantum confinement in amorphous dot analogous to those in the crystalline dot. Both experimental and theoretical approaches to address these issues would be worthwhile and desirable. Still the arena of amorphous quantum dots is beginning and many more issues of quantum confinement have to be addressed and investigated for the possible technological applications. The importance of residual stress in films demonstrated in this study has far reaching consequences regarding film properties and really cannot be ignored from the point of view of both basic and applied research. Much more to be done!!!