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Determination of surface structure and the depth profile of silica glass by infrared spectroscopy

C. Z. Tan^{1,2}

(1. *Laboratory of Solid State Microstructure and Department of Materials Science and Engineering, Nanjing University, 210093 Nanjing, China;*
2. *Institut für Mineralogie, Freie Universität Berlin, 14195 Berlin, Germany*)

Abstract: The surface structure and properties are different from those of the bulk, depending on the substrate materials and deposition condition, and playing an important role in precise optical components. The conventional spectroscopic methods to monitor the surface structure are restricted only in several layers of molecules. It is known that the penetration depth of the incident light increases with its wavelength and decreases with the angle of incidence. Thus infrared spectroscopy provides a powerful means for determination of surface structure and the depth profile up to micrometers. By recording the reflection spectra at different angles of incidence, the surface structure and its depth profile can be monitored successively. Further, the incident field has the subcomponents parallel and perpendicular to the surface, which excite the transverse and longitudinal optic modes, respectively. Change of the polarization direction of the incident light provides a practical function to study anisotropic property of the surface and the interaction between the transverse and longitudinal optic modes. In this work, infrared spectrophotometer was applied to investigate the depth profile in microstructure of silica glass. Combining with the glass fiber system, this technique can be used for in-situ control of the deposition process. In comparing with ellipsometry, this method reveals both structural and constitutional information.

Key words: surface structure; depth profile; infrared spectroscopy; silica glass

1 Introduction

The surface structure and physical properties of condensed matter and thin films are different from those of bulk. The gradient in microstructure can extend to micrometer depth, depending on the preparation processes and chemical species^[1-2]. The formation of surface layers is due to the corrosion reactions, diffusions, ion implantation and film deposition, exhibiting the depth profile in both microstructure and chemical composition. It has long been observed that at the Brewster angle of incidence on the pol-

ished glass surface, the reflected electric field component in the plane of incidence does never disappear completely, because of the surface layer structure^[3]. This plays an important role in application of optical components composed of glasses and in micro-lithography. The conventional analytical techniques (XPS, SIMS, nuclear techniques etc.) for surface structure are restricted only in several layers of molecules. On the other hand, almost all substances have the reflection bands in the infrared frequency region. The resonance frequency ($\omega^2 = k/m$, k : the force constant, m : the reduced mass) in the infrared range depends on the chemical species and mo-

lecular structure. Infrared reflection spectroscopy at near normal incidence thus provides the powerful means to probe the surface structure, depth profile, and gradient in chemical composition up to micrometer range^[4-6]. The main advantages of this method are due to the fact of rapid, inexpensive and nondestructive performance, without vacuum system and even in-situ condition. Further, the incident electric field has the subcomponents parallel and perpendicular to the surface, which excite the transverse (TO) and longitudinal (LO) optic modes, respectively. The resonance frequencies of the TO modes correspond to the peak positions in $\epsilon_2 = \text{Im}(\epsilon)$, where ϵ ($\epsilon = \epsilon_1 + i\epsilon_2$) is the complex dielectric function, while peaks in $-\text{Im}(1/\epsilon)$ reveal the resonance frequencies of the LO modes^[7-8]. In terms of the Kramers-Kronig analysis of near-normal infrared reflection spectrum, TO and LO splitting frequencies can be evaluated^[8]. Change of the polarization direction of the incident light therefore provides a practical function to study anisotropic property of the surface and the interaction between the TO and the LO modes.

Silica glass is an extensively investigated object, because of its scientific and technological importance. It has been observed that the distribution of Si-O-Si angles varies from the surface to the inside of the glass, because of different fictive temperatures^[1-2,9]. The vibration amplitude decreases with increasing penetration depth of the incident waves. On the other hand, the main TO (near $1\ 086\ \text{cm}^{-1}$) and the LO (near $1\ 265\ \text{cm}^{-1}$) modes of silica glass are associated with the asymmetric Si-O-Si vibrations, and the penetration depth decreases with increasing angle of incidence^[4-6,8]. The TO mode is mainly associated with the vibrations parallel to the sample surface, while the LO mode is related to the vibrations perpendicular to the sample surface. Study of the incident angle-dependent infrared reflection spectra can thus provide a useful method to probe the surface structure of glasses.

In this work, we report the application of infrared spectrophotometer to study the surface structure and its depth profile of silica glass.

2 Principle of the measurements

The physical basis for determination of the surface structure and the depth profile of glasses is due to the facts that the shifts in the infrared reflection peaks are associated with the change in the chemical composition and surface structure, and the penetration depth decreases with increasing angle of incidence. In the absorptive infrared range, the intensity of the incident light will drop by a factor e^{-1} after the wave has propagated a distance $d_p = \lambda(4\pi\kappa)^{-1}$, known as the penetration depth^[10-11], where λ is the wavelength of the incident light in vacuum, and κ is the extinction coefficient. The penetration depth d_p is therefore the function of the wavelength. For anisotropic materials, the two eigenmodes (ordinary wave; o-ray, and extraordinary wave; e-ray) have different extinction coefficients and thus different penetration depths for a given wavelength. Note that at oblique incidence, the penetration depth may be approximately expressed by $d_p \cos(\beta)$, here β denotes the complex angle of refraction^[10], as schematically shown in Fig. 1. The penetration depth is found to decrease with increasing angle of refraction (hence with the angle of incidence α ; $\sin(\alpha) = n_c \sin(\beta)$, n_c : the complex refractive index, $n_c = n + i\kappa$)^[10]. This feature provides the possibility to monitor the surface structure and its depth profile by recording the reflection spectra at different angles of incidence. In the case that the thickness of the sample is much larger than the penetration depth of the incident light, the reflection spectrum reveals only the surface layer information, namely the average spectrum over the distance of the penetration depth approximately. However, if the thickness of a thin film is much smaller than the penetration depth, the reflection spectrum

carries information from the film and the substrate^[11].

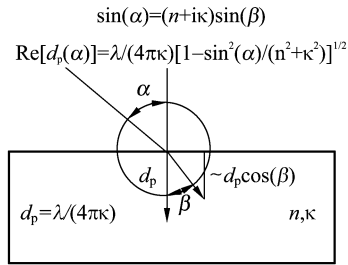


Fig. 1 Schematic depiction of the dependence of penetration depth on the angle of incidence α . The angle of refraction is a complex quantity in the absorptive frequency region. The penetration depth decreases with increasing angle of incidence.

Infrared radiation is normally absorbed only when the vibration mode has a change in dipole moment with a component perpendicular to the direction of propagation. In the case of transmission measurement, the density of state (DOS) of the LO mode is very small, because the propagation direction of the transmitted light is parallel to that of the incident wave, and the LO mode is normally infrared inactive under such a condition^[4]. For oblique incidence, however, the densities of state of the excited LO and the TO modes depend on the polarization state of the incident light, as schematically shown in Fig. 2. The electric field component (E_s) perpendicular to the plane of incidence only interacts with vibrations whose change in dipole moment has a component parallel to the sample surface, and thus only excites the TO modes, whereas the component (E_p) parallel to the plane of incidence has subcomponents of electric field vectors parallel and perpendicular to the sample surface, which can excite both TO and LO modes. Note that the direction of vector E_s is in general not parallel to the direction of vibrations of excited TO modes in anisotropic crystals^[13]. Change of the polarization direction of the incident light therefore provides a practical function to study

anisotropic property of the surface and the interaction between the TO and the LO modes.

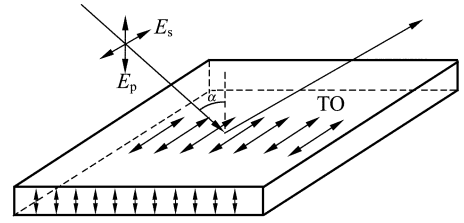


Fig. 2 Schematic depiction of vibrations of excited LO and the TO modes at oblique incidence. The electric field component (E_s) perpendicular to the plane of incidence only interacts with vibrations whose change in dipole moment has a component parallel to the sample surface, and thus only excites the TO modes, whereas the component (E_p) parallel to the plane of incidence has subcomponents of electric field vectors parallel and perpendicular to the sample surface, which can excite both TO and LO modes. Note that the direction of vector E_s is in general not parallel to the direction of vibrations of excited TO modes in anisotropic crystals.

3 Results

Fig. 3 shows the reflection spectra of silica glass (Suprasil W2, thickness 0.51 mm) at different angles of incidence, recorded by incidence of randomly polarized light (Perkin Elmer, Spectrum GX). All spectra reported in this work were obtained by averaging 100 scans of measurements. The resolution was selected to be 8 cm^{-1} . The thickness of the sample is much larger than the penetration depth of the incident light in this case. The spectra thus represent the average results of the surface layers. Near normal incidence, it is demonstrated that the incident field excites mainly the TO mode in the vicinity of 1122 cm^{-1} . The frequency ω_{TO} of the main TO mode is found to be independent of the angle of incidence. However, the ratio $R_{\text{LO}}/R_{\text{TO}}$ (R_{LO} : the reflectance of the main LO mode;

R_{TO} : the reflectance of the main TO mode), and the frequency ω_{LO} of the LO mode near $1\,265\text{ cm}^{-1}$ are shown to increase with increasing angle of incidence, as the results shown in Fig. 4. At large angles of incidence, the electric field excites both LO and TO modes.

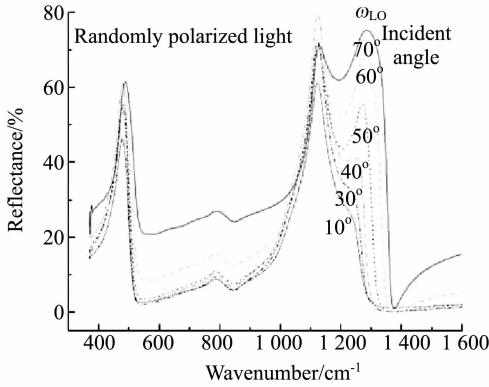
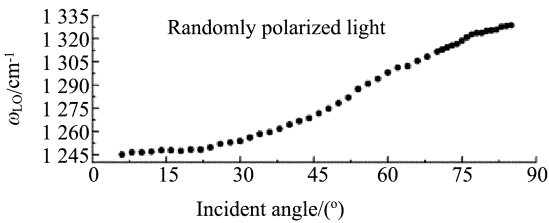
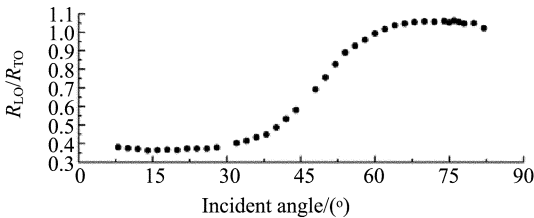


Fig. 3 Reflection spectra of silica glass (Suprasil W_2 , thickness 0.51 mm) at different angles of incidence, recorded by incidence of randomly polarized light. The reflectance and resonance frequency of the LO mode are found to increase with increasing angle of incidence.



(a)



(b)

Fig. 4 Dependence of ω_{LO} (a) and R_{LO}/R_{TO} (b) on the angle of incidence, evaluated by incidence of randomly polarized light.

The dependence of the reflection spectra on the azimuth angle of polarization direction of the incident light is shown in Fig. 5. The angle of incidence is set to be at 60° , and the azimuth angle of the polarization direction of the incident light ranges from 0° (the incident s-wave) to 90° (the incident p-wave). It is demonstrated that the reflection spectra of silica glass depend not only on the angle of incidence, but also on the polarization direction of the incident light. The frequency ω_{LO} in the vicinity of $1\,122\text{ cm}^{-1}$ remains a constant under different conditions. However the ratio R_{LO}/R_{TO} , and the frequency ω_{LO} near $1\,265\text{ cm}^{-1}$ is found to be the function of the angle of incidence and the polarization direction of the incident light, as the results shown in Fig. 6, and 7. A correlated effect of the polarization direction and the angle of incidence on the frequency ω_{LO} of the LO mode and on the ratio of R_{LO}/R_{TO} exhibit two opposite tendencies on two sides of a critical angle of incidence near 45° : below this critical angle both ω_{LO} and R_{LO}/R_{TO} increase with increasing azimuth angle of the polarizer, and above this angle they are found to decrease with increasing azimuth angle of the polarizer. Both ω_{LO} and R_{LO}/R_{TO} remain unchanged at different directions of polarization of the incident light at the critical angle of incidence. Note the facts that the incident electric field component perpendicular to the glass surface shows the same variation tendency with the angle of incidence as that of ω_{LO} and R_{LO}/R_{TO} , and the vibration amplitude of the surface bands is much larger than that of the bulk. Therefore we can draw a conclusion from these observations that vibrations of the LO mode are perpendicular to the surface of the glass, induced by electric field component in normal direction of the surface. These observations also indicate that there exist the surface layer structure and the depth profile in silica glass.

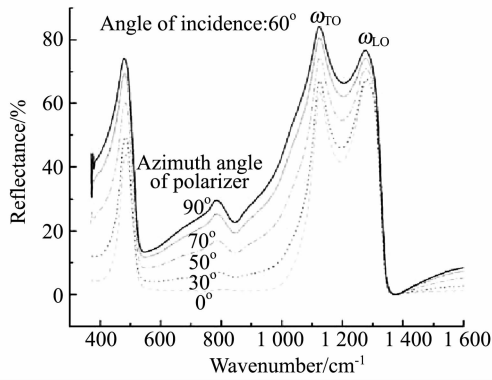


Fig. 5 Reflection spectra of silica glass recorded at different azimuth angles of polarization direction of the polarized incident light. The angle of incidence is at 60° .

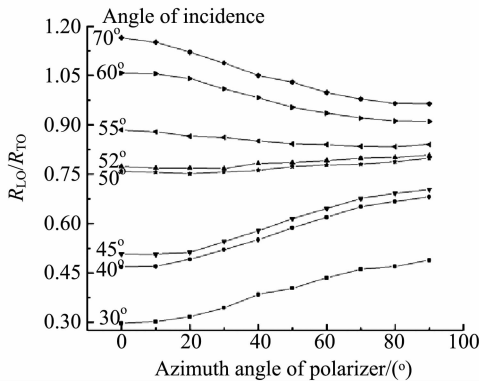


Fig. 6 Dependence of the ratio R_{LO}/R_{TO} on the azimuth angle of the polarizer at different angles of incidence.

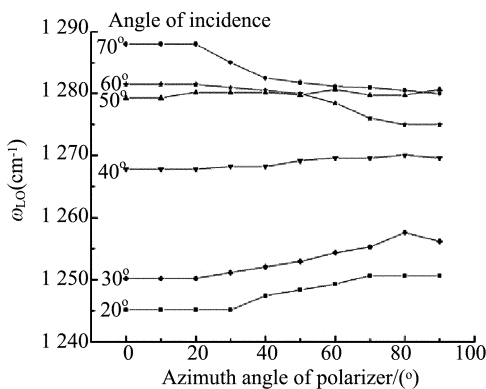


Fig. 7 Dependence of ω_{LO} on the azimuth angle of the polarizer at different angles of incidence.

4 Discussion

The penetration depth at normal incidence is given by $\lambda/(4\pi\kappa)$. However, at oblique incidence, the complex penetration depth may be changed into $\lambda/(4\pi\kappa)\cos(\beta)$, where β is the complex angle of refraction, given by the relation: $\sin(\alpha) = (n + i\kappa)\sin(\beta)$ (n : the refractive index). The real part of the penetration depth Red_p at oblique incidence is therefore expressed by^[10]

$$Red_p = \frac{\lambda}{4\pi\kappa} \sqrt{1 - \frac{\sin^2(\alpha)}{n^2 + \kappa^2}}, \quad (1)$$

The LO and the TO modes have different penetration depths, because of different indices of refraction and different extinction coefficients. Note that the frequency ω_{LO} depends on the angle of incidence α , as the result shown in Fig. 4. The calculated relationship between the penetration depths of the LO and the TO modes at different angles of incidence is shown in Fig. 8. The penetration depth of the TO mode is found to decrease weakly with increasing angle of incidence, whereas the penetration depth of the LO mode increases significantly with increasing angle of incidence. This result confirms that the LO mode is excited by the electric field component perpendicular to the surface of the glass,

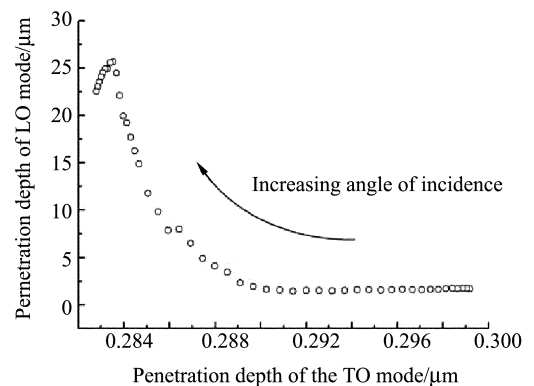


Fig. 8 Calculated relationship between the penetration depths of the LO and the TO modes at different angles of incidence.

vibrating in normal direction, and the excited TO mode vibrates perpendicular to the normal direction.

The frequencies of the principal infrared absorption bands reflect the modes of vibration of the amorphous network and are consequently directly related to the Si-O-Si bonding force constants on a local scale in silica glass. Long-range correlated vibrations are likely to be present only in a limited frequency range^[14]. The frequency ω_{TO} of the main TO mode near $1\,086\text{ cm}^{-1}$ is given by^[15]

$$m\omega_{\text{TO}}^2 = 2f_1 \sin^2\left(\frac{\theta}{2}\right) + 2f_2 \cos^2\left(\frac{\theta}{2}\right), \quad (2)$$

where f_1 is the central force constant ($\sim 600\text{ N/m}$), f_2 is the non-central force constant ($\sim 100\text{ N/m}$), m is the oxygen mass, and θ is the mean Si-O-Si bridging bond angle. Differing from crystalline state, the Si-O-Si bridging bond angle in silica glass distributes in a wide range^[16-17], with its mean value of $\sim 144^\circ$. According to the Lyddane-Sachs-Teller (LST) relation^[18]

$$\frac{\omega_{\text{LO}}^2}{\omega_{\text{TO}}^2} = \frac{\epsilon_s}{\epsilon_\infty}, \quad (3)$$

where ϵ_s and ϵ_∞ denote the static and optical dielectric constants, respectively, the ratio of $\omega_{\text{LO}}/\omega_{\text{TO}}$ is thus a constant ($\sim 1\,265/1\,086 = 1.165$, for silica glass) under different conditions. Hence the change in ω_{LO} and in ω_{TO} is associated with variation in the mean Si-O-Si bridging bond angle θ .

It is demonstrated that the frequency of the TO mode remains a constant at different azimuth angles of polarization of the incident light, indicating the molecular structure on the surface is isotropic, because the excited TO mode vibrates in the directions parallel to the glass surface. Therefore, TO mode reveals no information concerning the surface layer structure and its depth

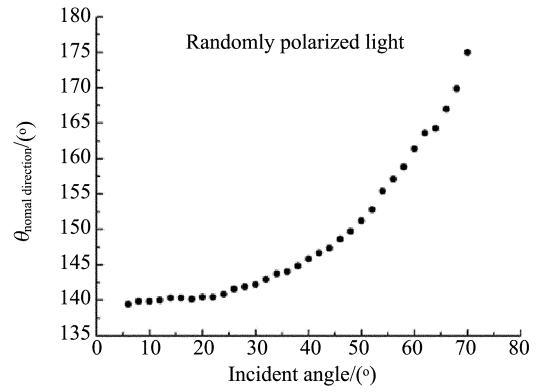
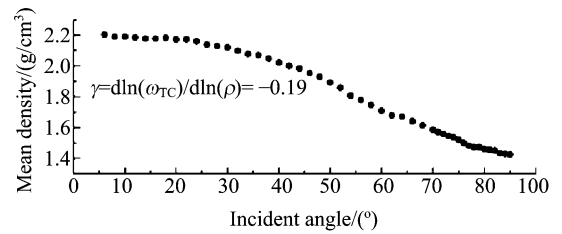
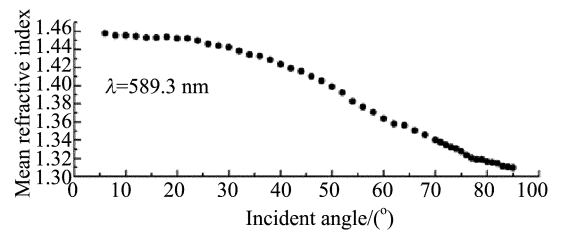


Fig. 9 Dependence of the mean Si-O-Si bridging bond angle θ in normal direction on the angle of incidence.



(a)



(b)

Fig. 10 Dependence of the mean density (a) and the mean refractive index (at $\lambda = 589.3\text{ nm}$) (b) of the layer structure in normal direction on the angle of incidence.

profile. However, the LO mode vibrates in the direction perpendicular to the glass surface. Variation in the frequency ω_{LO} and hence in ω_{TO} in the direction perpendicular to the glass surface indicates the change in the mean Si-O-Si bridging bond angle in normal direction. In terms of the evaluated values of ω_{LO} shown in Fig. 4, dependence of the mean Si-O-Si bridging bond angle θ in normal direction on the angle of incidence can be

calculated by Eq. (2), which is shown in Fig. 9. The mean Si-O-Si bond angle in normal direction varies from $\sim 140^\circ$ to $\sim 180^\circ$, as the angle of incidence changes from $\sim 0^\circ$ to 90° , showing the depth profile in microstructure of silica glass. In terms of the evaluated Grüneisen constant γ ($\gamma = -d\ln(\omega_{\text{TO}})/d\ln(V) = d\ln(\omega_{\text{TO}})/d\ln(\rho)$, V : the volume, ρ : the density) for the main TO mode^[19-21] from permanently densified silica glasses ($\gamma = -0.19$), we can even quantitatively estimate the mean density of the layer structure in normal direction by incident angle-dependent ω_{LO} (and hence ω_{TO}), as the result shown in Fig. 10 (a). It is demonstrated that the density decreases with increasing angle of incidence, indicating that the surface layer is the less dense structure. From the relationship between the refractive index and density ($n = 1.037 + 0.191 \rho$, at $\lambda = 0.5893 \mu\text{m}$) of densified silica glasses^[22-24], we can further calculate the mean refractive index of the surface layer structure at different angles of incidence, as the result shown in Fig. 10 (b). The monitored surface layer structure may play an important role in application of precise optical components composed of silica glass and in micro-lithography. In terms of the glass fiber system, we may apply the infrared spectrophotometer for in-situ monitoring deposition condition of thin films.

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5 Conclusions

In terms of the infrared reflection measurements, TO-LO splitting was monitored in silica glass at oblique incidence. The resonance frequency ω_{LO} of the main LO mode was found to depend on the angle of incidence and polarization direction of the polarized incident light, whereas the resonance frequency ω_{TO} of the main TO mode remains a constant under different conditions. The excited TO mode vibrates in the directions parallel to the glass surface, and the LO mode vibrates in the direction perpendicular to the glass surface, excited by the electric field component in normal direction. Variation in the frequency ω_{LO} and hence in ω_{TO} in the direction perpendicular to glass surface indicates the change in the mean Si-O-Si bridging bond angle in this direction, the depth profile in microstructure of silica glass. In terms of the evaluated shift in ω_{LO} with the angle of incidence and the mode Grüneisen constant, the density of the surface layer was calculated, indicating the less dense structure on the surface.

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Brief professional biography of the author:

Prof. Dr. hail. C. Z. Tan

Since Jan. 01, 2001; Professor of the Nanjing University (Cheung Kong Scholar Professor, Ministry of Education, People's Republic of China).

Since Mar. 01, 2000; Priv. Doz. of the Freie Universität Berlin (Institut für Mineralogie).

Oct. 01, 1994-Feb. 16, 2000; Habilitand of the Freie Universität Berlin (Habilitation stipendiary, DFG).

Working areas: propagation of light in glass fiber, anisotropic crystals, and optical sensors (for vibration, displacement, and acceleration measurements), structure and properties of densified glasses.

Habilitation: Effects of Pressure, Temperature and Wavelength of the Incident Light on the Refractive Index of Silica Glass.

Publication title: The Refractive Index of Silica Glass and Its Dependence on Pressure, Temperature, and Wavelength of the Incident Light, Chap. 2, p. 51-90, in: Silicon-Based Materials and Devices, Vol. 2, ed. H. S. Nalwa, Academic Press, 2001.

Habilitation lecture: Lichtleitung in Glasfasern (Guided waves in glass fiber), Freie Universität Berlin, Feb. 16, 2000.

Sep. 01, 1993-Sept. 30, 1994; Post-doctoral researcher at the Institut für Physik (under the guidance of Prof. O. Kanert), Universität Dortmund (DFG-stipendiary, Graduiertenkolleg Festkörperspektroskopie).

Research areas: NMR, dielectric and optical relaxations in amorphous materials and optical thin films.

Oct. 01, 1990-Aut. 31, 1993; Wissenschaftlicher Mitarbeiter and Doktorand at the Institut für Mineralogie (under the guidance of Prof. J. Arndt), Freie Universität Berlin.

Research areas: structural relaxations in densified glasses and optical thin films.

Dissertation: Structural Relaxation in Vitreous B₂O₃ and Densified SiO₂ Glass.

Promotion on May 13, 1993.

Oct. 01, 1986-Dec. 30, 1989; Assistant researcher of the Institute of Geochemistry, the Chinese Academy of Sciences.

Working areas: phase equilibrium, optical properties of oxides at high pressures and high temperatures.