CHAPTER-5

ESR STUDY

5.1 Electron Spin Resonance

“Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR) is a physical method of observing resonance absorption of microwave power by un-paired electron spins in a magnetic field. ESR was discovered by Zavoisky in 1945 for transition metal ions in salts and developed after world war-II using advances in microwave and solid-state electronics”.[4] The fundamentals of the technique, its parameters and methods of interpreting the results are discussed.

5.2 Electron spin

“Classically an electron considered to be negatively charged, rotating sphere. This rotation produces a circulating current in the direction opposite to the rotation of the sphere. The circular current produces a magnetic field in the vicinity of the electron. Therefore, the electron spin (self-rotation) can be considered equivalent to a tiny magnet”[4] ,**Fig-5.1**. Such magnets form magnetically neutral pairs in atoms and molecules.

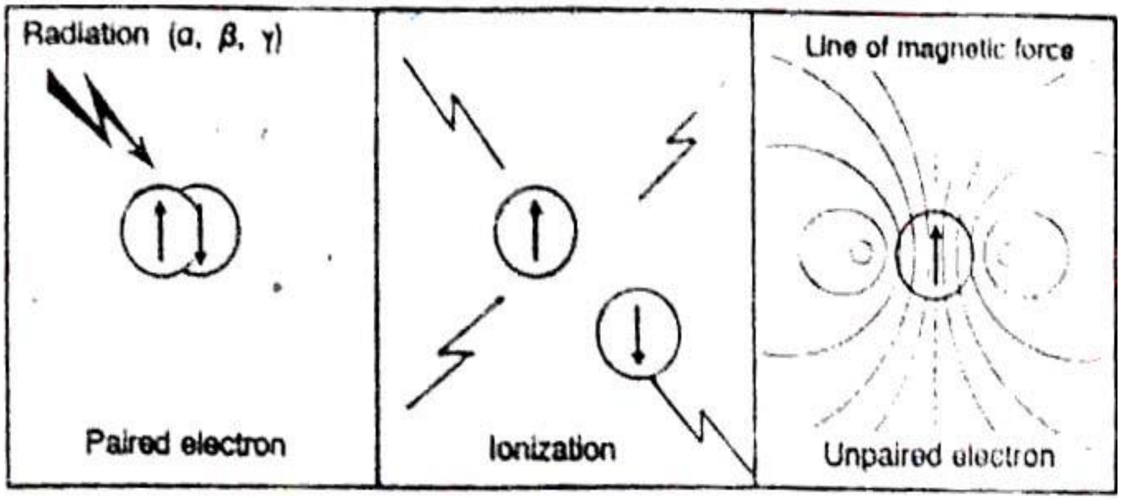

Fig:5.1 (i) Paired electron and radiation (ii) Ionization (iii) Formation of unpaired electrons.

No net magnetic moment is present due to the neutralizing effects of the pairing of electron spins in most materials. Natural or artificial radiation ionizes atoms or molecules, i.e. breaks the paired electron.

When some other atoms trap the ionized electron, an electron-excess atom and an electron-deficient atom are formed: the former and the latter, both with an unpaired electron, are called “trapped electron” and “trapped hole” center, respectively. They now have net magnetic moment μ_e due to the unpaired electron spins. An unpaired electron may be considered as a tiny magnet. Unpaired spins tend to align parallel to the direction of a magnetic field and magnetize. Hence the word “electron paramagnetism” is used for magnetic properties arising from unpaired electrons in a material. They are detectable with microwave absorption spectroscopy under an external magnetic field called “Electron Paramagnetic Resonance (EPR)” or “Electron Spin Resonance (ESR)”.

5.3Fundamental principle of ESR

“When spinning electrons are placed in an external static magnetic field, the direction of a small magnet, i.e., the direction of spin rotation which is initially random becomes either the same or opposite to that of the external magnetic field.”[4]

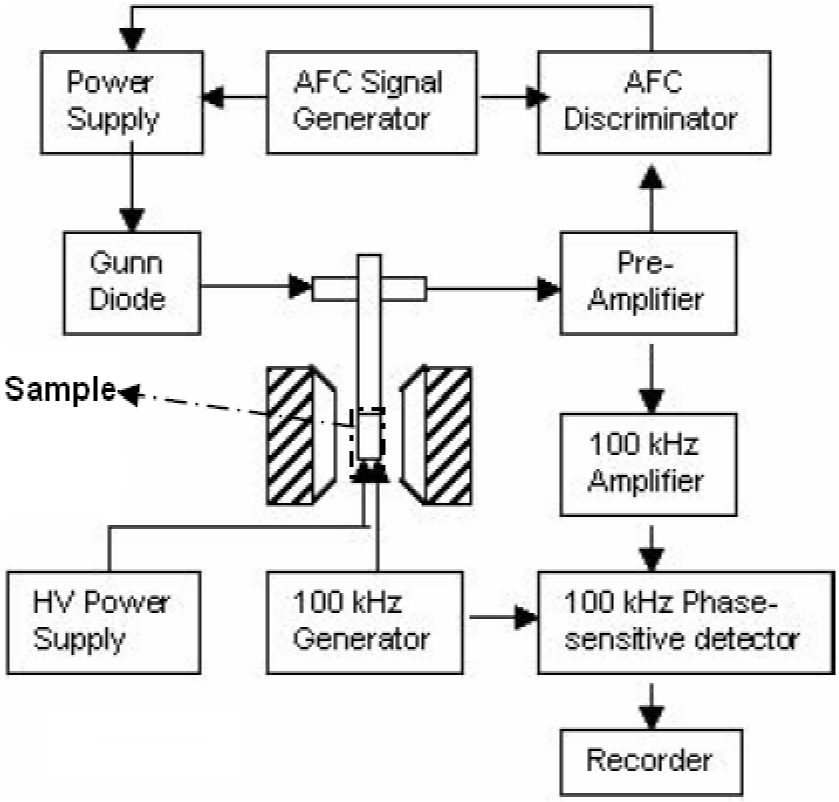

Fig5.2 Block Diagram of ESR set-up

These two situations are energetically different and are called ‘up spin’ and ‘down spin’ states. The electron spins excited from the lower energy level by the absorption of the microwave quanta flop to the lower level by the lattice vibration in a time called the spin lattice relaxation time T_1 . Flopping of the spins also occurs due to the interaction among spins and this flopping time is called the spin-spin relaxation time T_2 . If the microwave power is so high as to pump out the spins in the lower level or the relaxation time is too long for the population to be restored, a decrease in signal intensity is observed. This is called “saturation”. The magnetic properties of unpaired electrons are expressed by following parameters.

- Spin angular momentum: $S = \frac{h}{2\pi}$; h is Planck constant
- Spin quantum number: $S = \frac{1}{2}$; for an electron
- Magnetic quantum number: $M = \pm\frac{1}{2}$ are allowed
- Bohr Magneton: B the basic units of a small factor magnet for an electron spin.
- Magnetic moment $\mu : \mu = \mu_e = -gBS$
- Spectroscopic splitting factor $g = 2.0023$ for free electron.
- H in Tesla $1\,Tesla = 10^4\,Gauss$

5.4 ESR spectra and parameters

- Line shape: Gaussian and Lorentzian shapes
- g -factor
- Anisotropic g-factors and random orientation.
- Hyperfine hf structure
- Proton hyperfine structure: Equivalent-protons
- McConnell’s Relation
- Superhyperfine (shf) structure
- Fine Structure

***g* factor:** “The spectroscopic splitting factor, the g-factor of an ESR signal, is an important parameter, since unpaired electrons in different environments have slightly different g-factors, resulting in the appearance of signals for different centers at different magnetic field strengths. Classically, the slight g-factor change due to the environment might be ascribed to the change of the effective negative charge by the spread of the electron wave function”.[4] The g -factor is determined by,

$$g = \left(\frac{h}{B}\right)\left(\frac{\nu}{H}\right) = 71.455 \times \frac{\nu}{H}$$

Where, the microwave frequency ν (in GHz) and magnetic field H (in mT) are measured with a frequency counter and a field meter, respectively. The g-factor of the unknown signal is determined using a standard signal with a known g -factor. If resonance of standard signal with g_1 and unknown signal with g_2 occurs at H_{01} and H_{02} respectively (the magnetic field separation $\Delta H = H_{01} - H_{02}$, the resonance condition gives

$$g_1 H_{01} = g_2 H_{02} = \frac{h\nu}{B}$$

$$g_2 = \frac{g_1 H_{01}}{H_{02}} = \frac{h\nu}{B}$$

$$g_2 = \frac{g_1 H_{01}}{H_{01} - \Delta H} = \frac{h\nu}{B}$$

$$g_2 = \frac{g_1}{1 - \frac{\Delta H}{H_{01}}} = \frac{h\nu}{B}$$

Usually, the resonance field (H_0), falls around 340 mT for ν = 9.4 GHz

ESR signal is defined by the “g -factor” and hence the g-factor are generally around 2.0 and are usually determine to the decimal place with a probable error of 0.0002 ~ 0.0005.

Now a brief account of defects patterns in SiO_2, which are identified by ESR technique, is presented in following discussions.

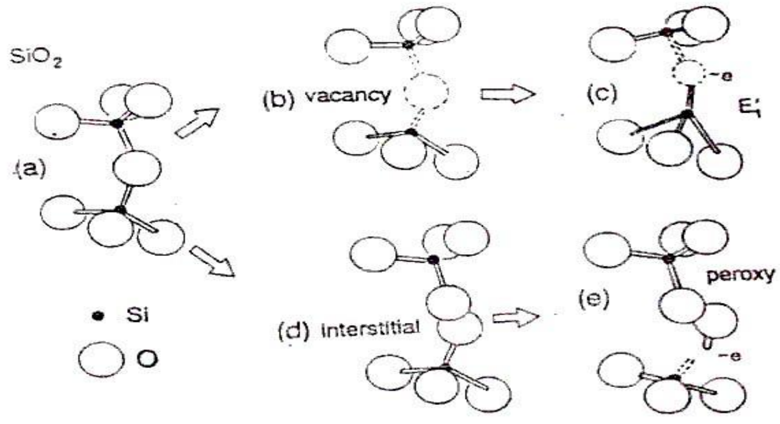

Fig-5.3: Defects paired in SiO_2(a) normal SiO_2 lattice (b) Oxygen Vacancy [V^-] (c) E_1' center (d) Interstitial O^{-2} (e) paroxy center

Normal Lattice: $[S_iO_4]^0, {S_iO_4}^{-4} \ or \equiv S_i - O - S_i$

(a) Intrinsic Defects

E₁' center : $[S_iO_3]^+, {S_iO_3}^{-3} \ or \ \equiv S_i \cdot S_i \equiv$

Peroxy center : $[S_iO_5]^-, {S_iO_5}^{-5} \ or \ \equiv S_i - O(-O^{\cdot}) - S_i \equiv$

$g_1 = 2.0014, g_2 = 2.0074, g_3 = 2.0067$

NBOHC : $[S_iO_4]^+, {S_iO_4}^{-3} \ or \ \equiv S_i - O^{\cdot}$

$g_1 = 2.0010, g_2 = 2.0095, g_3 = 2.078$

OHC(${O_3}^-$?) : $O - O - O^{\cdot}$

$g_1 = 2.011 - 2.012$

Oxygen Vacancies: $[S_iO_3]^+, {S_iO_3}^{-3}$ or $[V^-]^{+2}$, $[S_iO_3]^0, {S_iO_3}^{-4}$ or $[V - 2e]^0$

The following three pairs are considered in S_iO_2 **Fig-5.3 (a** to **e)**. A pair oxygen vacancy [V-] and interstitial O^{-2} is not stable at room temperature. '**b**' and '**d**'. A paired E₁' center (an electron at an Oxygen vacancy) and peroxy center (interstitial $O^{\cdot}$) is stable and is observed in natural quartz and irradiated amorphous-S_iO_2. '**c**' and '**e**'. A paired Si vacancy and Si interstitial is energetically not stable. A paired anion (O^{-2}) vacancy and cation (Si^{+4}) vacancy called "Schottky Pair" is negligible around room temperature unless S_iO_2 is quenched from high temperature. The detail information about E₁' and Ge center are only presented as it is related with the present work.

E₁' Center:

$g_1 = 2.00179, g_2 = 2.00053, g_3 = 2.0030$

Model: The simplest point defect in quartz is an electron at the oxygen vacancy called the E₁' center. The model for the E₁' center in amorphous and crystalline S_iO_2 is an unpaired electron in a dangling sp^3 hybrid orbital of pyramidal ${S_iO_3}^{-3}$ where an oxygen ion O^- is extracted from a S_iO_4 tetrahedron. The production of the E₁' center is shown in **Fig-5.3** '**a**' to '**c**'.

Thermal Property: The signal intensity of E₁', center is increased above 200 °C at the expense of the hole type Al-center. It is annealed about at 360 °C to 380 °C and regeneration efficiency is strongly reduced by annealing at 500 °C. Presumably, high temperature annealing annihilates oxygen vacancies around dislocations or in α-recoil tracks. From the annealing and saturation properties, two types of E_1', centers have been proposed, one is annealed around 200 °C in an artificially irradiated sample, while the other is stable up to around 360 °C.

Microwave Power dependence: The signal intensity of the E_1' center is easily saturated at a microwave power of 10^{2} mW.

(b) Impurity-Associated Defects

Al-center: Al-related hole center –

$[AlO_4]^0, [Al^{+3}h^+]^0, AlO_4{}^{-4}, = Al - O^{\cdot}$

Ge-center: Ge-related electron center –

$[GeO_4/L_i]_c^0,\ [Ge^{+4}e^-/Li^+]_c^0, GeLiO_4^{-4}(= Ge - O^-)^- - Li^+$

Ti -center: Ti -related electron center –

$[TiO_4/L_i]_A^0, [Ti^{+4} - e^-/Li^+]_A^0, TiLiO_4^{-4}$ or $(= TiO^-) - Li^+$

ESR spectra of natural crystalline-S_iO_2 powder show signals associated with impurities. Electron (or hole) trapped by impurities gives ESR signals associated with impurities such as substitutional tetravalent ions (Ge^{+4} and Ti^{+4}) and trivalent ion (Al^{+3}) as well as interstitial monovalent cation,

(M^+, Li^+ and Na^+). ESR spectra of the Al-related hole center and Ge and Ti -related electron centers in natural crystalline S_iO_2.

Ge Center

$[GeO_4/L_i]_c^0 : (M = Li)$

$g_1 = 2.0000, g_2 = 1.9973, g_3 = 1.9962$

Model: Isoelectronic Ge^{+4} substitutes for a Si^{+4}site the S_iO_2 lattice but its electrons affinity (ionization potential) is considerably larger, resulting in trapping of an electron created by ionizing irradiated to form $[GeO_4 - e^-]^-$ in the S_iO_2 lattice. The total charge of the center is -1 and thus Ge^{+3} at a Si^{+4} site in an S_iO_2 structure has a negative effective charge attracting an interstitial monovalent cation M^+

M^+ such as H^+, Li^+ of Na^+ to form stable $[GeO_4/M^+]^0$ at room temperature. The process is summarized as follow.

Ge^{+4} (irradiation) (stabilized by M^+ at RT)

$[SiO_4]^0 \rightarrow [GeO_4]^0 \rightarrow [GeO_4 - e^-]^- \rightarrow [GeO_4 - e^-/M^+]^0$

ESR signal of the Ge center appears at the high field side of the E_1 ' center.

Microwave power dependence. The Ge center saturated at high microwave power (>100mW). Ge center is annealed out at 250 °C – 280 °C[1].

5.5 Results and Discussion

The ESR spectra are recorded for synthetic quartz material to confirm the availability of centers in material which may support to discussion over the changes in TL glow curve and OSL decay curve pattern under influence of different physical conditions. The finer grain of 63-53μm was subjected to 1KGy gamma irradiation and the ESR spectra is recorded at room temperature by Varian E-112 E-line Century series ESR spectrometer with 100kHz field modulation. The Tetracyanoethylene (TCNE, $g = 2.00277$) was used as a standard for the g -factor measurement.

The following series of experiments were conducted:

1.ESR recorded at room temperature for unannealed sample followed by different gamma doses: spectra-I

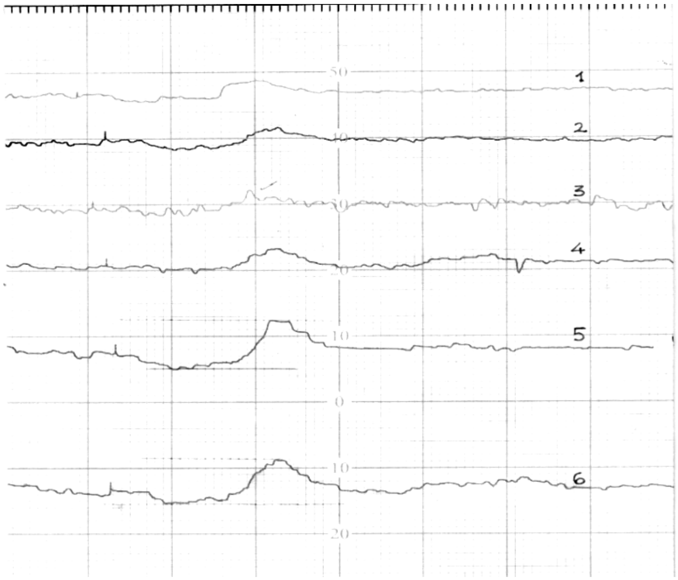

Fig 5.4 ESR spectra-I

ESR spectra of unannealed sample followed by different gamma doses.

(1) unannealed; 0.1mW (2) unannealed, 20 Gy and 0.1mW (3) unannealed, 5mW (4) unannealed, 20 Gy, 5 mW (5) unannealed, 320 Gy, 0.1mW (6) unannealed, 320 Gy, 5mW.

2. ESR recorded at room temperature for unannealed and 600°C annealed sample followed by 1000 Gy gamma dose: spectra-II.

Fig 5.5 ESR Spectra-II

ESR spectra of unannealed and 600 °C sample followed by 1000 Gy gamma dose.

(1) unannealed, 0.1mW (2) unannealed, 5mW (3) unannealed, 100 Gy, 5mW (4) 600 °C annealed, 0.1mW (5) 600 °C annealed, 5mW.

3. ESR recorded at room temperature for 400 °C and 1000 °C annealed samples: spectra-III and IV

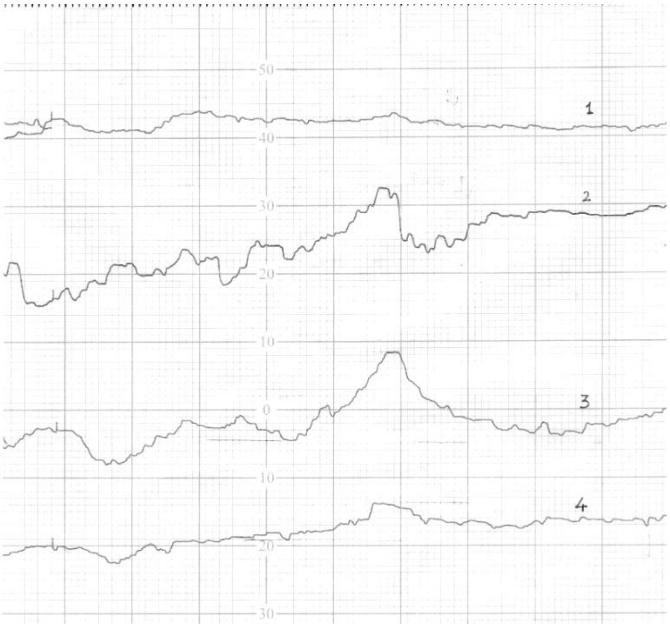

Fig 5.6 ESR Spectra-III

ESR spectra recorded at room temperature for 400 °C and 1000 °C annealed samples followed by gamma dose of 1000 Gy.

(1) 400 °C annealed, 0.1mW (2) 400 °C annealed, 5mW (3) 1000 °C annealed,5mW (4)1000 °C annealed, 0.1mW.

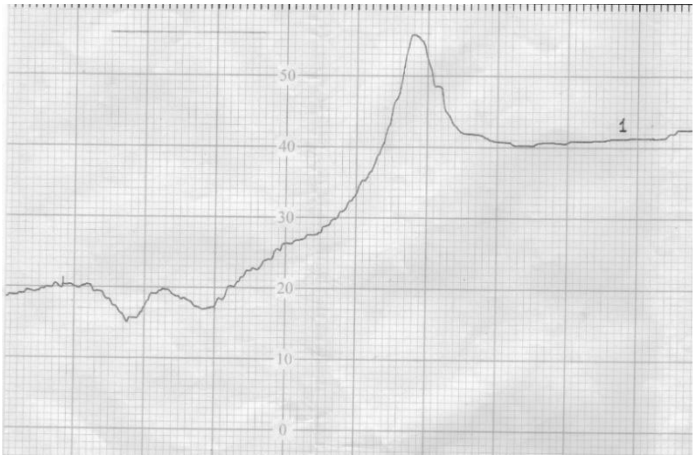

Fig 5.7 ESR Spectra-IV

ESR spectra recorded at room temperature for 1000 °C annealed samples followed by gamma dose of 1000 Gy

4. ESR recorded at room temperature before UV illumination for E_1' center of unannealed and annealed sample followed by gamma dose of 1000 Gy: spectra-V(a) and V(b)

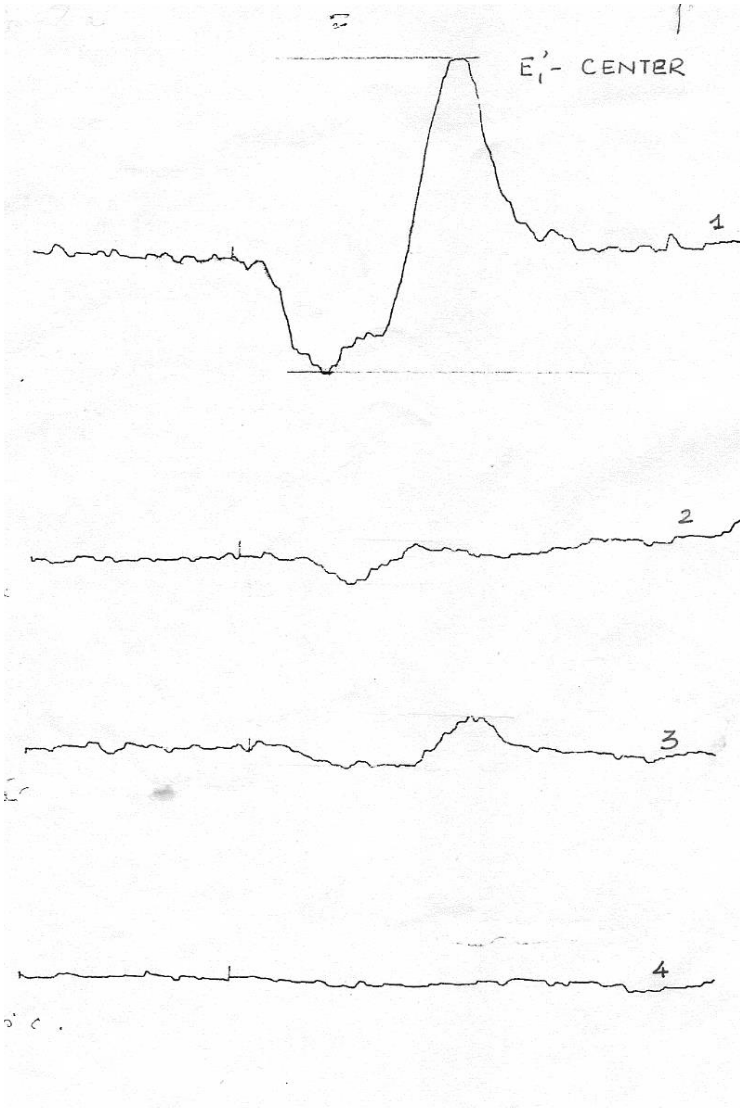

Fig 5.8 ESR Spectra-V(a)

ESR recorded at room temperature before UV illumination for E_1' enter of unannealed and annealed sample (1000^0C, 400^0C and 600^0C)followed by gamma dose of 1000 Gy.

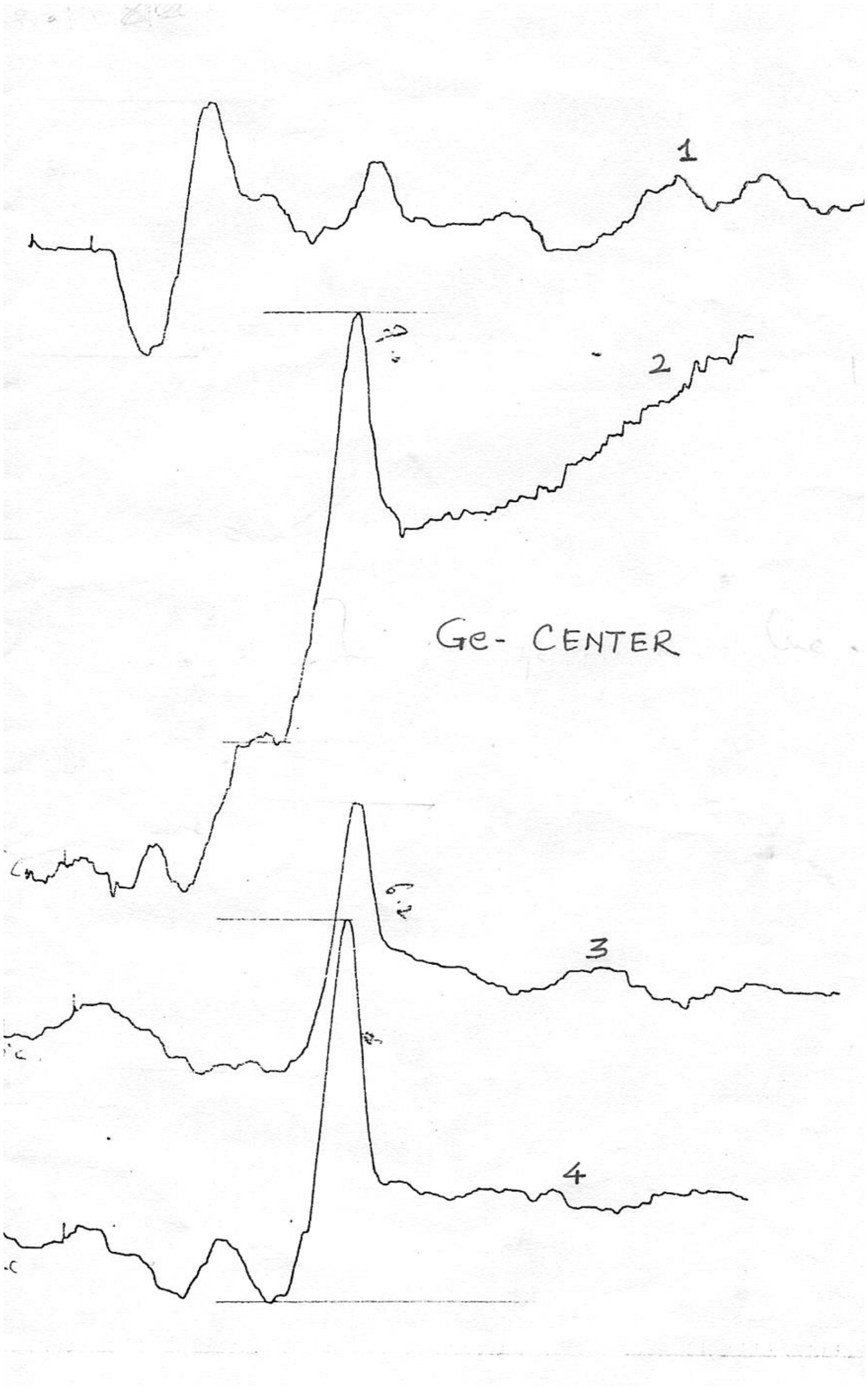

Fig. 5.9 ESR Spectra-V(b)

ESR recorded at room temperature before UV illumination for Ge center of unannealed and annealed (1000^0C, 400^0C and 600^0C) sample followed by gamma dose of 1000 Gy.

5. ESR recorded unannealed and annealed sample followed by UV bleaching (spectra-VI(a) and VI(b)).

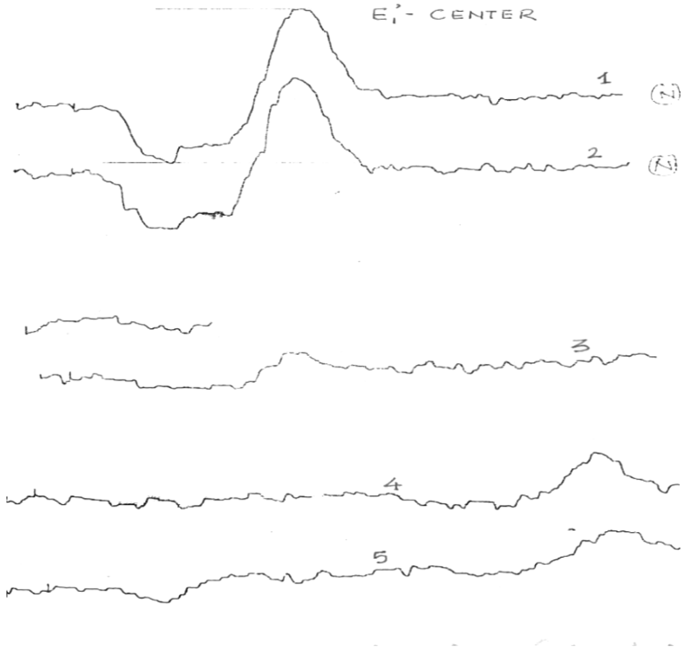

Fig. 5.10 ESR Spectra-VI(a)

ESR recorded at room temperature after UV illumination for E_1’ center of unannealed and annealed (400^0C, 600^0C and 1000^0C)sample followed by gamma dose of 1000 Gy.

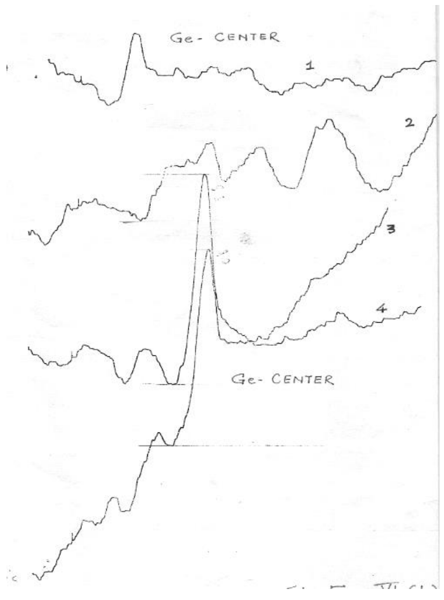

Fig. 5.11 ESR Spectra-VI(b)

ESR recorded at room temperature after UV illumination for Ge center of unannealed and annealed (400^0C, 600^0C and 1000^0C)sample followed by gamma dose of 1000 Gy.

ESR spectra recorded at room temperature for the unannealed sample followed by gamma exposures, its show a center exhibiting an axially systematic g-tensor. The amplitude of this center saturated for a microwave power above 0.1mW, (it is clear from the ESR data for 5mW). The amplitude of this center grows with given dose. The center has been assigned to E_1' center namely on the basis of the observed g-value and microwave power dependence. The observed *g* values (~2.0017) for the present work were reasonably consistent with the ones previously reported by Jani et al., (g = 2.0018, 2.0005, 2.0003) and P.G.Benny et al[1,2]

The ESR results reported that the growth in TL and OSL sensitivity with increase in dose under identical physical conditions. Further, thermally untreated materials were exposed to high gamma dose of 1000 Gy. It was noticed that along with the saturation in center for higher microwave power, ESR signal enhances. (Spectra-I, II, III and IV).

Here, it was noticed that the specimens annealed at 400^0C exhibits weaker E_1' signal as compared to unannealed sample, however it was also observed that a new center was exhibited at higher microwave power (~5mW). That center has been suggested to be Ge center. Again, it is mainly on the basis of observed g-values in the present work and corresponding well established report by the others[3]

On further investigations it is pointed out that the ESR signal corresponding to this center grows with the increase in temperature of annealing. This center doesn't saturate up to 5mW microwave power.

To understand and correlate the bleaching/charge transfer effects on the center, the ESR spectra were recorded before and after the sun exposure of the specimens for thermally untreated as well as pre-heat treated at elevated temperatures. It was observed that the amplitude of E1' center reduces remarkably from 6.1 to 4.6a.u after the sun exposure for thermally untreated, 1000 Gy dose specimens (spectra-V(a) and VI(a)). But this center disappears in annealed sample beyond 600^0C, even before sun exposures (spectra-V(a)).

To resolve the Ge center, the ESR was recorded for 5mW microwave power under similar experimental conditions. Such center shows reduction in ESR signal for thermally untreated specimen, whereas significant enhancement is observed in these centers from

6.1 to 8.2 and 6.7 to 7.7a.u for 600°C and 1000°C annealed specimens before and after UV illumination respectively (spectra-V(b) and VI(b)).

The thermally untreated material shows saturation with a very low ESR signal compare to annealed material which is attributed to effect of pre-thermal treatment, such treatment is responsible for changes in OSL/TL properties of quartz specimen. From present investigation of ESR study it is concluded that the E_1' and Ge centers play predominant role in the production of TL peaks at 110°C and 220°C. Bleaching study of ESR signal indicate that the reduction of E_1' center and growth of Ge center are correlated with enhancement of 210°C-230°C TL peak in material after optical stimulation. Thus, ESR spectra strongly correlate with TL glow curve pattern and OSL properties of synthetic quartz.

References

1. Jani et al., “Further characterization of the E_1’ center in crystalline SiO_2”, Physical Review B 27,2285-2293, 1983.

2. P.G.Benny et al., “The E_1’ center and its role in TL sensitization in quartz”, Radiation Measurements 35, 369-373, 2002.

3. Motoji Ikeya, Zimmerman, “New application of electron spin resonance”, World Scientific Publications.

4. New Applications of Electron Spin Resonance, Introduction to ESR: What is Electron Spin Resonance (ESR) ? pp. 23-66 (1993)