KRAMERS-KRONIG ANALYSIS OF INFRARED REFLECTANCE SPECTRA WITH A SINGLE RESONANCE

S. S. NG[1*], Z. HASSAN[2] & H. ABU HASSAN[3]

Abstract. In this study, a Kramers-Kronig (KK) analysis program has been compiled. The use of the KK method to analyze the normal incidence infrared (IR) reflectance spectra with a single resonance has also been described. To verify our program, spectra generated by a damped single harmonic oscillator model were analyzed, in which the optical parameters were known. Our results show that, the values of optical phonon modes, i.e. w_{TO} and w_{LO}, obtained by this computational technique are in good agreement with the values used in the simulation model. The average errors are sufficiently small, i.e. about 0.67% and 0.25% for w_{TO} and w_{LO} respectively.

Keywords: Kramers-Kronig analysis, infrared reflectance spectroscopy, optical phonon modes

Abstrak. Dalam kajian ini, satu program analisis Kramers-Kronig (KK) telah dikompilasikan. Penggunaan kaedah KK untuk menganalisis spektrum pantulan inframerah pada sinar tuju normal dengan resonans tunggal juga telah dihuraikan. Bagi mengesahkan program ini, analisis spektra yang dihasilkan daripada model getaran harmonik ringkas terlembap telah dilakukan dengan parameter-parameter optikal yang diketahui. Keputusan menunjukkan bahawa nilai-nilai fonon bermod optik, iaitu w_{TO} dan w_{LO} yang diperolehi daripada kaedah pengiraan ini adalah bersepadan dengan nilai yang digunakan dalam model simulasi. Purata ralat adalah kecil, iaitu sekitar 0.67% dan 0.25% bagi w_{TO} dan w_{LO} masing-masing.

Kata kunci: Analisis Kramers-Kronig, pantulan infra-merah spektroskopi, fonon bermod optik

1.0 INTRODUCTION

The Kramers-Kronig (KK) method has long been used to analyze the reflection spectra to obtain various optical parameters of materials [1-15]. This can be due to it being easier to develop and can be applied to analyze a wide variety of materials (organic to inorganic, solid to liquid, and single crystal, polycrystalline, and amorphous) without reference to specific models. However, the application of the KK method was hindered by its complexity of the integration.

Recently, there has been great interest in the KK method to analyze the IR reflectance spectra of various materials. This is driven by the widely used of Fourier transforms infrared (FTIR) spectroscopy in the semiconductor industry for material

[1,2&3]School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia. Tel.: 604-6533673, Fax: 604-6579150
*Corresponding author: shashiong@yahoo.com

characterization. In addition, modern computing power now permits KK method to be used in reflectance spectra analysis even for sophisticated KK transformation, since calculations are now fast and inexpensive.

The purpose of the present study is to develop a KK analysis program to analyze infrared (IR) reflectance spectra obtained from our homemade IR spectroscopy system. Subsequently, it will be used (in our future study) to analyze reflectance spectra of advanced materials, i.e. wide band gap III-V semiconductor materials, such as gallium nitride (GaN). Hence, the use of the KK method to analyze IR reflectivity data will be described in details. The validity of the KK program is checked with spectral simulation derived from a damped single harmonic oscillator model. Finally, the errors of transverse optical (TO) and longitudinal optical (LO) phonons mode (i.e. w_{TO} and w_{LO} values) obtained by KK analysis program is estimated by comparing with the values used in the simulation model.

2.0   IR SPECTRAL SIMULATION

The normal incidence reflectivity $R(w)$ from the front surface of an infinitely thick crystal of complex refractive index $\tilde{n}(w)$ is given by:

$$R(w) = \left[\frac{\tilde{n}(w)-1}{\tilde{n}(w)+1}\right]^2 = \left[\frac{\sqrt{\tilde{\varepsilon}(w)}-1}{\sqrt{\tilde{\varepsilon}(w)}+1}\right]^2 \tag{1}$$

Here $\tilde{\varepsilon}(w)$ is the complex dielectric function of the material and is related to $\tilde{n}(w)$ by the following relationship:

$$\sqrt{\tilde{\varepsilon}(w)} = \tilde{n}(w) \tag{2}$$

In this work, the $R(w)$ were generated with a Lorentz model for a damped single harmonic oscillator model [16]:

$$\tilde{\varepsilon}(w) = \varepsilon_\infty + \frac{Sw_{TO}^2}{w_{TO}^2 - w^2 - iw\gamma} \tag{3}$$

Here ε_∞, w_{TO}, S and γ represent the high frequency dielectric constant, the transverse optical-phonon frequency, the phonon oscillator strength and the phonon damping respectively. The phonon oscillator strength S is given by:

$$S = \varepsilon_\infty \left(\frac{w_{LO}^2}{w_{TO}^2} - 1\right) \tag{4}$$

Here w_{LO} is the longitudinal optical-phonon frequency.

The simulated IR spectra then were subjected to our KK analysis program to obtain the phase $\varphi(w)$ and the associated optical and dielectric constants.

3.0 KRAMERS-KRONIG ANALYSIS

The phase change φ at a particular wavenumber w between the incidence and the reflected signal is obtained from the KK dispersion relation [17]:

$$\varphi(w) = -\frac{w}{\pi} \int_0^{\infty} \frac{\ln R(w') - \ln R(w)}{w'^2 - w^2} dw' \tag{5}$$

The spectrum of $\varphi(w)$ is then utilized to obtain the real (n) and imaginary (k) parts of the complex refractive index $(\tilde{n}(w) = n(w) + ik(w))$ by using:

$$n(w) = \frac{1 - R(w)}{1 + R(w) - 2\sqrt{R(w)} \cos\varphi(w)} \tag{6}$$

$$k(w) = \frac{2\sqrt{R(w)} \sin\varphi(w)}{1 + R(w) - 2\sqrt{R(w)} \cos\varphi(w)} \tag{7}$$

Consequently, the real (ε') and imaginary (ε'') parts of the complex dielectric function $(\tilde{\varepsilon}(w) = \varepsilon'(w) + i\varepsilon''(w))$ can be obtained by using:

$$\varepsilon'(w) = n(w)^2 - k(w)^2 \tag{8}$$

$$\varepsilon''(w) = 2n(w)k(w) \tag{9}$$

In this work, the KK analysis program was written in Turbo Pascal. Detailed discussion of the procedures of integration and extrapolation for KK analysis is given below.

4.0 INTEGRATION AND EXTRAPOLATION OF KK TRANSFORM

As the reflectance cannot be measured over an infinite wavenumber range, the data must be extrapolated in some manner into the unknown regions (i.e. especially in high wavenumber region), in order to calculate the integration of KK transform in Equation (5). Several extrapolation approaches have been evaluated and reported [1, 3, 15, 17-19]. In most cases, the common ways to evaluate the $\varphi(w)$ are (i) integrate the KK transform over a wide spectral range by simulating or extrapolating the reflectivity beyond the cutoff of the experimental data based on formula given by Philipp *et al.* [1] and Stern [3] and (ii) integrate the KK transform from a restricted range in which the reflectivity is known over a wavenumber range $w_1 \leq w \leq w_2$, and is assumed constant outside this range. In this study, the method that we have used is based on the latter approach.

According to Roessler [15], method of evaluation of $\varphi(w)$ from a short region of a reflection spectrum can give reliable results as compared to the method used to

analyze the data over a much wider spectral range. This approach have been used and evaluated by Abdullah *et al.* [18]. It has shown that precise and useful data can be obtained by this technique. Since this method was fairly easily applicable compared to other methods, hence, our KK analysis program was written based on this approach. Detailed discussion about this approach is given below.

The KK transform in Equation (5) can be expressed under the following form, which is more convenient to calculate the $\varphi(w)$.

$$\varphi(w) = -\frac{1}{2\pi}\int_0^\infty \frac{d}{dw'}\left[\ln R(w') - \ln R(w)\right]\ln\left|\frac{w'-w}{w'+w}\right|dw' \tag{10}$$

This expression shows that (i) the spectral regions in which the reflectance is constant and (ii) the values of $R(w)$ in the spectra regions such as $w' \ll w$ or $w' \gg w$, do not contribute to the value of $\varphi(w)$. Thus in practice only a small portion of the spectrum associated with the absorption band system is required to calculate $\varphi(w)$. As an example, for absorption in IR due to lattice vibrations, the major contributions to $\varphi(w)$ are from reststrahlen region and neighborhoods of this region. Since the reflectivity is changing rapidly in these regions, hence the function $\frac{d}{dw'}\left[\ln R(w') - \ln R(w)\right]$ is large. Therefore, for IR study, the contribution to the phase shift from the system in the extreme ultra-violet (UV) may safely be neglected [15].

The integral of Equation (10) is evaluated by representing $\ln R(w')$ by straight-line segments between points [20]. Error introduced by this approach is minimized by sampling the segments at 0.25 cm^{-1} wavenumber intervals, i.e. by introducing 4 points between points from the reflectance data.

For every KK transformation, computer assumes constant reflectivity in the wavenumber region from 0 to w_1 cm^{-1} and w_2 cm^{-1} upwards. Here, the w_1 and w_2 are the lower and upper wavenumber for the simulation reflectivity spectra. It should be noted that using Turbo Pascal programming, with this resolution, it can only contain up to ~2000 cm^{-1}, due to the limitation of memory size.

5.0   DETERMINATION OF OPTICAL PHONON MODE

For IR study, the optical phonons (LO and TO) are the frequencies of interest for describing the optical interactions with the lattice. Typically, these interactions will lead to a characteristic reststrahlen band, i.e. the reflectance increases sharply caused by the resonance of transverse optical phonon (TO) and decreases at the resonance of the longitudinal optical phonon (LO). As an example, Figure 1 shows typical single resonance spectra of $R(w)$, $n(w)$ and $k(w)$ for (a) an ideal case, i.e. $\gamma = 0$ and (b) for non-ideal case, i.e. $\gamma \neq 0$ in IR region. From these figures, the IR reststrahlen band of material is mainly characterized by w_{TO} and w_{LO}.
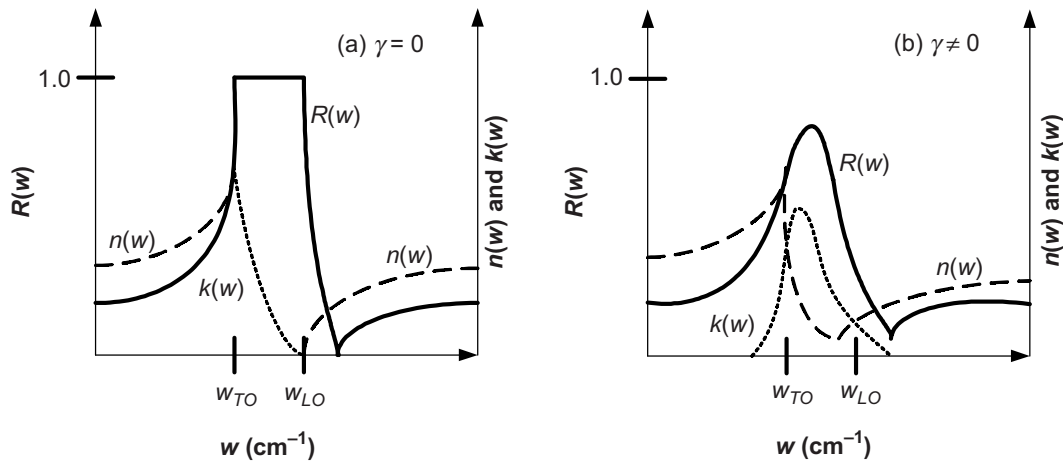
Figure 1   Typical single resonance spectra of $R(w)$, $n(w)$ and $k(w)$ for (a) an ideal case, i.e. $\gamma = 0$ and (b) for non-ideal case, i.e. $\gamma \neq 0$ in IR region

Through the KK approach, the transverse optical (TO) and longitudinal optical (LO) phonons mode may also be obtained without reference to any model of dielectric response. From the above discussion, once the phase $\varphi(w)$ value is obtained, the optical and dielectric constants can be determined by using numerical calculation of Equation (6) to Equation (9). Consequently, the TO and LO mode can be easily determined from the maximum position of ε'' and from the peak position of $\mathrm{Im}(-1/\varepsilon)$ curves, respectively.

6.0   RESULTS AND DISCUSSION

In this study, a KK analysis program has been developed. In order to check the validity of this method and to estimate the error in the obtained optical phonon modes, the KK program was applied to an isotropic model (i.e. a very simple case namely spectra with a single resonance). All the calculations have been done on an Intel Pentium III 500 MHz processor computer and with Window 98 second edition version. For KK integration, typical running time for one set of data is about 30 – 60 seconds.

Based on Equation (3), several simulated IR reflectivity spectra, i.e. CsI, CdTe, ZnSe, InP and AlP were derived. The dispersion parameters used to generate the simulated spectra were taken from the reported values [16, 21, 22]. The dispersion parameters used for simulation are listed in Table 1 and their simulated spectra are shown in Figure 2.

As mentioned previously, $\varphi(w)$ was evaluated from a restricted range in which the reflectivity is known over a wavenumber range $w_1 \leq w \leq w_2$ and is assumed constant outside this range. The spectral range $w_1 \leq w \leq w_2$ used during integration

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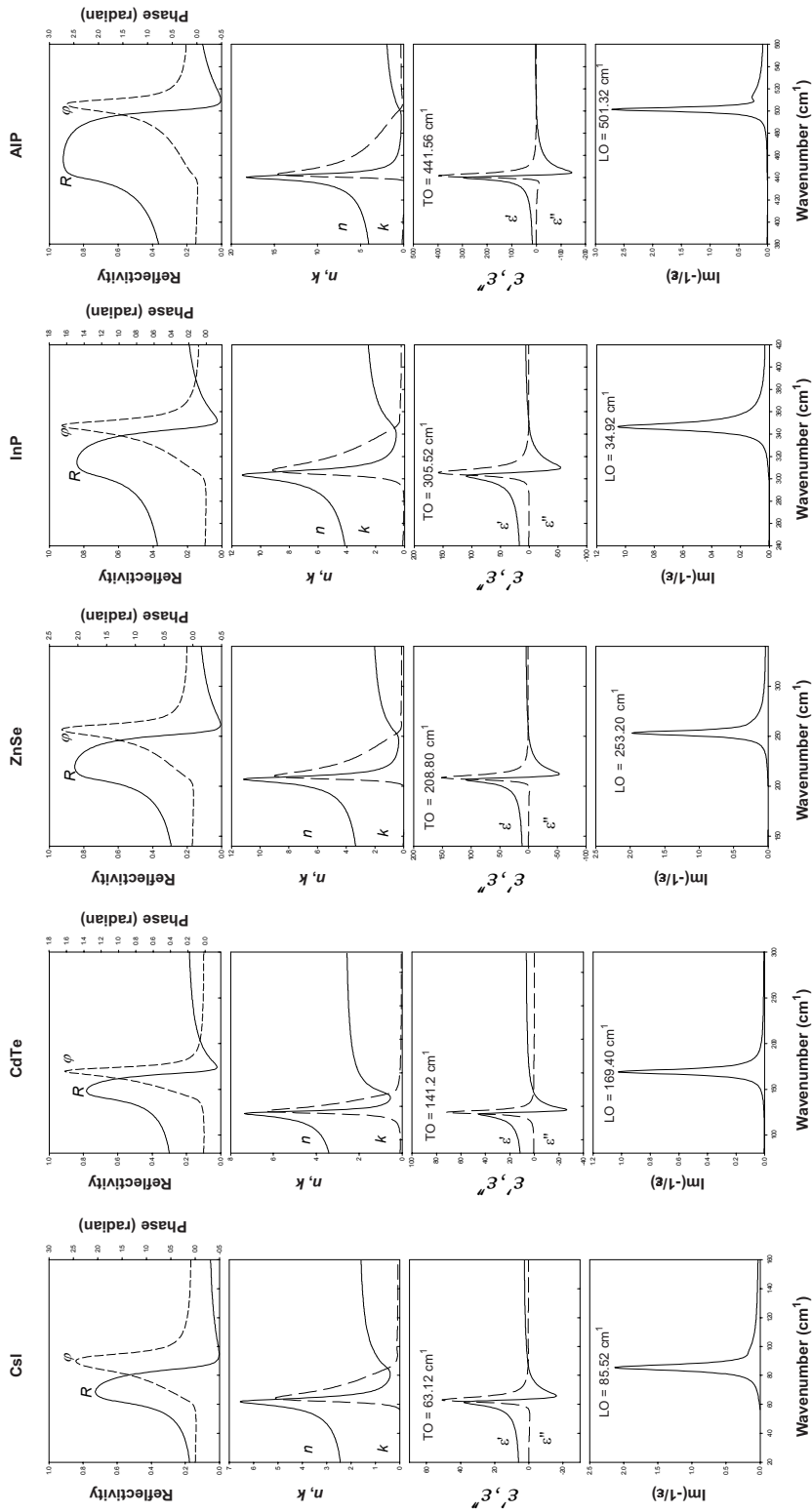
Figure 2 The simulation reflectivity spectra and the spectra of $\varphi(w)$, $n(w)$, $k(w)$, $\varepsilon'(w)$, $\varepsilon''(w)$ and $\mathrm{Im}(-1/\varepsilon)$ for CsI, CdTe, ZnSe, InP and AlP. The spectra of $R(w)$ were simulated by a damped single harmonic oscillator model. The spectra of $\varphi(w)$, $n(w)$, $k(w)$, $\varepsilon'(w)$, and $\varepsilon''(w)$ were obtained by the numerical calculation on the spectra of $\varepsilon''(w)$. The plots of $\mathrm{Im}(-1/\varepsilon)$ were obtained from the KK analysis. Features indicated on the spectra of $\varepsilon''(w)$ and $\mathrm{Im}(-1/\varepsilon)$ are assigned as transverse optical (TO) and longitudinal optical (LO) phonons modes

Table 1   The IR spectra dispersion parameters for isotropic materials in single form

Crystal	Dispersion parameters						Reference
	ε_0	ε_∞	S	$\gamma\,(\mathrm{cm}^{-1})$	$w_{TO}\,(\mathrm{cm}^{-1})$	$w_{LO}\,(\mathrm{cm}^{-1})$	
CsI	5.65	3	[a]2.64	[b]5	62	85	[21]
CdTe	10.2	7.10	3.10	6.63	141	[a]169	[16]
ZnSe	8.8	5.9	2.9	6.5	207	[a]252.81	[16]
InP	12.46	9.61	2.85	8	304	[a]346.16	[16]
AlP	9.83	7.56	[a]2.24	[b]5	440	501	[22]

[a] Derived using oscillator strength, i.e. $S = \varepsilon_\infty \left(\dfrac{w_{LO}^2}{w_{TO}^2} - 1 \right)$

[b] This value was chosen arbitrarily

for KK analysis is shown in Table 1. From the KK analysis, the obtained spectra of $\varphi(w)$ are shown together with the corresponding $R(w)$ spectra in Figure 2.

Based on the spectra of $R(w)$ and $\varphi(w)$, the spectra of $n(w)$, $k(w)$, $\varepsilon'(w)$ and $\varepsilon''(w)$ were then obtained by the numerical calculation. These spectra are shown also in Figure 2. In addition, the spectra of $\mathrm{Im}\,(-1/\varepsilon)$ which were obtained by the numerical calculation based on the spectra of $\varepsilon''(w)$ is also shown in Figure 2. The values of w_{TO} and w_{LO} determined from the maximum position of ε'' and from the peak position of $\mathrm{Im}\,(-1/\varepsilon)$ respectively were indicated inside the corresponding spectra. Table 2 summarized all the values of w_{TO} and w_{LO} obtained from KK analysis. The errors of w_{TO} and w_{LO} are also calculated, i.e. by using $\Delta w_{TO} = w_{TO}$ (Modeling) $- w_{TO}$ (KK) and $\Delta w_{LO} = w_{LO}$ (Modeling) $- w_{LO}$ (KK).

Table 2   Summary of the values of w_{TO} and w_{LO} obtained from KK analysis and the errors of Δw_{TO} and Δw_{LO}

Crystal	$w_{TO}(\mathrm{cm}^{-1})$		Δw_{TO}*		$\Delta w_{LO}(\mathrm{cm}^{-1})$		Δw_{LO}[#]	
	From KK analysis	From modeling	cm^{-1}	%	From KK analysis	From modeling	cm^{-1}	%
CsI	63.12	62.00	−1.12	1.806	85.52	85.00	−0.52	0.612
CdTe	141.20	141.00	−0.20	0.142	169.40	169.00	−0.40	0.237
ZnSe	208.80	207.00	−1.80	0.870	253.20	252.81	−0.39	0.154
InP	304.52	304.00	−0.52	0.171	346.92	346.16	−0.76	0.220
AlP	441.56	440.00	−1.56	0.355	501.32	501.00	−0.32	0.064

* $\Delta w_{TO} = w_{TO}$ (Modeling) $- \Delta w_{TO}$(KK)

[#] $\Delta w_{LO} = w_{LO}$ (Modeling) $- \Delta w_{LO}$(KK)

From Table 2, it can be seen that all the values obtained by the KK analysis are always larger than the values used in the simulation model. However, the average errors for the values of w_{TO} and w_{LO} are sufficiently small, i.e. about 0.67% and 0.25% respectively. While, the largest discrepancy for the w_{TO} and w_{LO} is only about 2 cm^{-1} and 1 cm^{-1} respectively.

Overall, a very good agreement is obtained between our KK analysis program and the simulation model. The discrepancies are believed to be due to the inherent nature of the KK integral itself (as mentioned in the previous section) and rounding errors in the simulation of $R(w)$ and the computation of $\varphi(w)$. It is important to note that the accuracy of the KK analysis strongly depends on the magnitude of $R(w)$. Hence, the error caused in $R(w)$ will lead to an inaccurately calculated phase and the associated optical and dielectric parameters.

In this work, the small estimated errors also implied that reliable results could be obtained through the evaluation of $\varphi(w)$ from a short experimental range of a reflection spectrum. Therefore, for the IR studies, the reflectance data outside the IR range can be neglected.

Finally, all results have shown that the KK analysis program has been successfully developed and can be used to analyze the IR reflectance spectra with a single resonance. Further studies are under way to extend the applicability of the KK program towards the experimental IR reflectance data, IR spectra with multiple resonances and polarized IR reflectance data.

7.0   CONCLUSIONS

We have presented a detailed description of the use of Kramers-Kronig (KK) method to analyze the normal incidence infrared (IR) reflectance spectra. In addition, a KK analysis program has been developed in this study. The validity of the KK program has been examined by comparing the values of the w_{TO} and w_{LO} with the values used by the simulation model and a good agreement has been obtained. The average errors are sufficiently small, i.e. about 0.67% and 0.25% for w_{TO} and w_{LO} respectively. Finally, these results show that the KK analysis program has been successfully developed and can be used to analyze the IR reflectance spectra.

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