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Autor: Kline, James S. / Pollak, Fred H. / Cardona, Manuel
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2. Zusatz: Eine einparametrige Gruppe von kanonischen Transformationen $\mathcal{M}' \to \mathcal{M}'$ die jedes α_k invariant lässt, ist von der Gestalt

$$\Phi_t: \quad p \to p' = p; \quad q \to q' = q + t\,\partial H/\partial p \quad (\mathrm{mod}\ 1)$$

wobei H nur eine Funktion von $p_1, \ldots, p_n$ ist. Die infinitesimale Erzeugende L von Φ_t ist durch $L(f) = [H, f]$ gegeben. L ist also ein *exakt kanonisches* Vektorfeld.

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Electroreflectance in Ge — Si Alloys[1])

by **James S. Kline**[2]), **Fred H. Pollak** and **Manuel Cardona**[3])
Physics Department, Brown University, Providence, Rhode Island, USA

(10. V. 68)

Abstract. The electroreflectance spectra of a series of germanium-silicon alloys, ranging in concentration from 6.5 atomic percent silicon to 92.4 percent silicon, have been measured in the energy region 0.8 eV–4.5 eV. A linear concentration dependence has been observed for all of the structures (E_0, $E_0+\Delta_0$, E_1, $E_1+\Delta_1$, E_0', $E_0'+\Delta_0'$ and E_2) that were investigated. A value of 4.00 ± 0.05 eV for the $\Gamma_{25}'-\Gamma_2'$ gap in pure silicon has been obtained from an extrapolation of the concentration dependence of the direct edge (E_0). It has also been observed that the E_1 and E_0' doublets of germanium merge into the 3.4 eV (E_0') structure of silicon. These results are compared to conventional reflectivity measurements.

I. Introduction

Considerable insight concerning the energy band structure of pure germanium and pure silicon has been gained by careful studies of the composition dependence of the properties of the germanium-silicon alloy system. Braunstein, Moore and Herman [1] were able to observe the transition between a [111] (germanium) and [100] (silicon)

[1]) Work supported by the National Science Foundation and the U.S. Army Research Office, Durham.
[2]) Presently in the Physics Department, Cornell University, Ithica, N.Y.
[3]) Alfred P. Sloan Research Fellow.

conduction band minimum from an investigation of optical absorption in such an alloy system. They also measured the concentration dependence of the direct edge to 12 atomic percent silicon, from which an estimate of the $\Gamma'_{25} - \Gamma'_2$ gap in silicon was made (this transition has not been observed directly). From magnetic susceptibility measurements BUSCH and VOGT [2] evaluated effective masses for the above mentioned conduction band minima and the valence band maxima. Information about the band structure above the fundamental edge has been obtained from the reflectivity studies of TAUC and ABRAHAM (TA) [3] and SCHMIDT [4].

Recently several modulation techniques have been developed [5–14] which greatly increase the resolution of optical spectra and enhance critical-point structure with respect to structureless background. At present electroreflectance provides the best sensitivity and resolution of the several techniques available for optical measurements on semiconductors above the fundamentals absorption edge. In particular the resolution and sensitivity are much better than those obtained by conventional reflectivity measurements. Using the electrolyte technique [12–14] the electroreflectance spectra of a series of germanium-silicon alloys, ranging in concentration from 6.5 percent silicon to 92.4 percent silicon, were measured in the energy region of 0.8 eV–4.5 eV. A linear concentration dependence has been observed for all of the structures (E_0, $E_0 + \Delta_0$, E_1, $E_1 + \Delta_1$, E'_0, $E'_0 + \Delta'_0$ and E_2) that were investigated. A value of 4.00 $\pm$ 0.05 eV for the $\Gamma'_{25} - \Gamma'_2$ gap in pure silicon has been obtained from an extrapolation of the concentration dependence of the direct edge (E_0). We find that the E_1 and E'_0 doublets of germanium merge into the 3.4 eV (E'_0) structure of silicon, indicating that both [100] and [111] transitions may be responsible for this structure. These results are compared to the reflectivity measurements of TA [3] (E_1 doublet) and SCHMIDT [4] (E'_0 structure). The E_2 peak is found to vary only slight with silicon composition. For this structure a doublet, similar to that seen for pure silicon in reflectivity [15] and electroreflectance [14], has been observed for the alloy with 92.4 percent silicon.

II. Experimental Details

The relative concentrations of the thirteen germanium-silicon alloy samples we have investigated were determined from density measurements and are listed in Table I. These samples all had polycrystalline structure and most were p-type. Homogeneity was verified by performing electroreflectance measurements at several different points on the sample surface: the E_0 structure was found to vary by less than 0.05 eV. For most samples a squarewave modulating voltage of 2 volts peak-to-peak was used with the sample biased 1 volt negative with respect to the electrode. For samples Ge-Si-11, Ge-Si-12 and Ge-Si-13 slightly higher voltages (6 volts a.c. and 3 volts d.c.) were used. All measurements were made at room temperature unless otherwise indicated.

III. Results

Shown in Figure 1 is the electroreflectance spectrum of sample Ge-Si-2 (10.9 percent silicon). The sign of ΔR is that observed when the positive cycle of the modulating voltage is applied to the sample. The overall features of this spectrum are similar to those of germanium [5, 13, 14, 16]. The band structure of germanium,

Table I

Silicon concentration and energies (in eV) of the peaks observed in the electroreflectance spectra of the thirteen germanium-silicon alloys measured. All data listed were taken at room temperature unless otherwise indicated.

Sample	Atomic percent silicon	E_0	$E_0+\Delta_0$	E_1	$E_1+\Delta_1$	E_0'	$E_0'+\Delta_0'$	E_2
Ge	0	0.800[b])	1.082[b])	2.12[c])	2.34[c])	3.13[c])	3.32[c])	4.42[c])
Ge-Si-1	6.45	1.042	1.297	2.205	2.390	3.170	3.328	4.389
Ge-Si-2	10.9	1.126	1.381	2.233	2.423	3.178	3.326	4.403
Ge-Si-3	16.2	1.319	1.569	2.305	2.483	3.204	3.378	4.386
Ge-Si-4	22.6	1.503	1.740	2.367	2.550	3.219	3.360	4.381
Ge-Si-5	34.7	1.914	2.118[d])	2.520	2.698	3.232		4.366
Ge-Si-6	45.7	2.245	2.387[d])	2.668	2.820	3.221		4.375
Ge-Si-7	45.8	2.238	2.379[d])	2.654	2.800	3.225		4.335
Ge-Si-8[a])	54.4			2.777	2.932	3.194		4.364
Ge-Si-9	64.0					3.282		4.385
Ge-Si-10	65.5			3.010		3.262		4.388
Ge-Si-11	76.6			3.058		3.253[e])		4.339
Ge-Si-12	76.8			3.064		3.255[e])		4.342
Ge-Si-13	92.4					3.310		4.345, 4.552
Si	100					3.32[c])		4.31, 4.51[c])

[a]) n-type. [b]) Reference [13]. [c]) Reference [14].
[d]) Obtained from an extrapolation of low temperature ($-30\,°C$ to $-78\,°C$) measurements.
[e]) In this concentration region the E_0 doublet crosses E_0' (see Fig. 4).

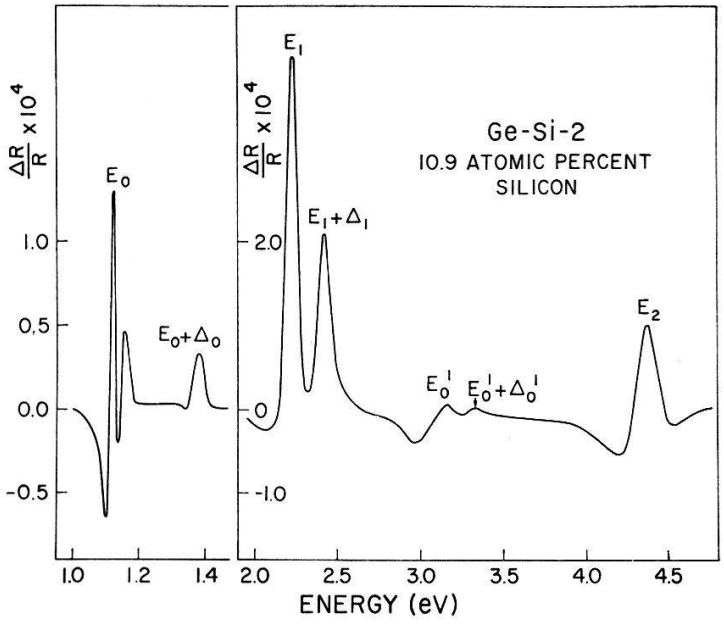

Figure 1

Electroreflectance spectrum of sample Ge-Si-2 at room temperature. In this and all subsequent figures the sign of ΔR is that observed when the positive cycle of the modulating voltage is applied to the sample.

including spin-orbit splittings, as obtained from a full-zone $\boldsymbol{k} \cdot \boldsymbol{p}$ calculation [17, 18] is shown in Figure 2.

The first structure seen in the spectrum (E_0, $E_0 + \Delta_0$) is caused by transitions at Γ between the spin-orbit split valence band (Γ_{25}') and the lowest-lying conduction band (Γ_2') [9, 19]. They are seen also in transmission but have not been resolved in the reflection spectrum. Above the direct edge there is a second set of peaks labelled E_1 and $E_1 + \Delta_1$. In germanium they have been shown to originate from transitions in the [111] direction of the Brillouin zone between the spin-orbit split Λ_3 valence band and the Λ_1 conduction band [19, 20]. There is some experimental evidence to indicate that this critical point occurs about one-third of the way across the zone [19]. Band structure calculation [17, 21–23] for germanium reveal an M_1-type critical point in this region of the zone.

The next structure seen in the electroreflectance spectrum (E_0', $E_0' + \Delta_0'$) occurs between 3.1 eV and 3.3 eV. Similar structure has been observed in electroreflectance

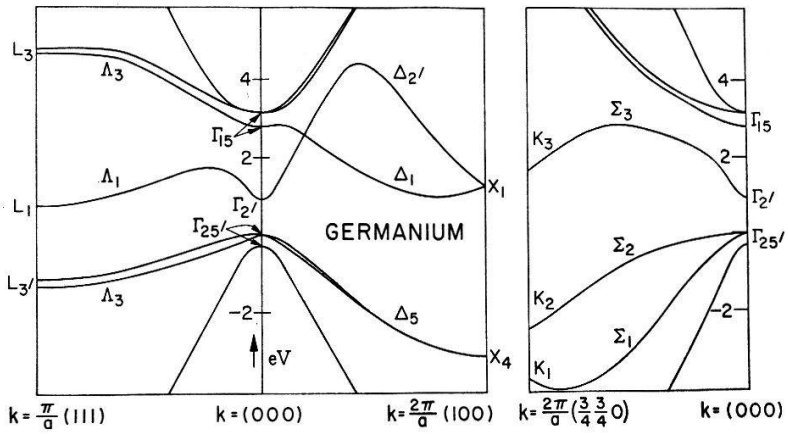

Figure 2

Band structure of germanium, including spin-orbit splittings, as obtained by the $\boldsymbol{k} \cdot \boldsymbol{p}$ method (see References [17] and [18]).

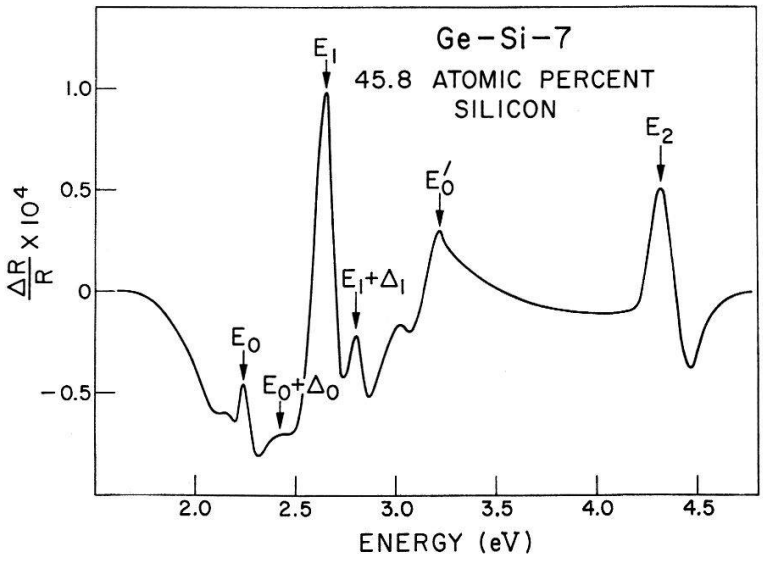

Figure 3

Electroreflectance spectrum of sample Ge-Si-7 at room temperature.

studies of a number of zincblende-type semiconductors [14, 24]. A shoulder in conventional reflectivity is observed at about this energy. SCHMIDT has studied the silicon concentration dependence of this reflectivity structure. There is some experimental evidence which indicates that $\Delta_5 - \Delta_1$ transitions near Γ (see Fig. 2) are responsible for this doublet: for germanium and a number of zincblende-type materials there is good agreement between the experimentally determined value of Δ_0' and theoretical calculations of the spin-orbit splitting of the Δ_5 valence band near $k = 0$ [14].

In the region 4.2 eV–4.5 eV an s-shaped curve is observed in the spectrum. This structure corresponds to the large peak seen in reflectivity at 4.45 eV in germanium. Band structure [17, 21–23] and optical constants [21, 23, 26–28] calculations indicate that E_2 is caused by clusters of critical points near X and K and along Σ (see Fig. 2).

The electroreflectance spectrum of Ge-Si-7 (45.8 percent silicon) is plotted in Figure 3. A comparison of this figure and Figure 1 shows that as silicon is added to germanium the E_0 and E_1 doublets increase in energy and that there is a decrease in

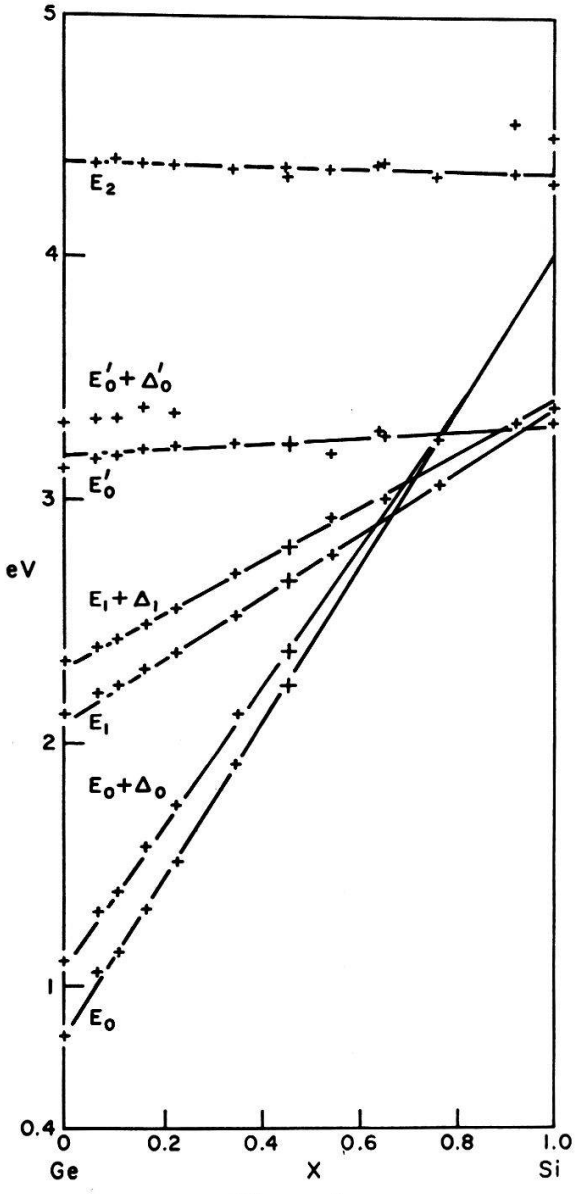

Figure 4

Energies of the various structures investigated as a function of silicon concentration.

Δ_0 and Δ_1. The $E_0 + \Delta_0$ structure, which is not sharply defined at room temperature, is seen more clearly at low temperatures (— 78 °C). The E_0' and E_2 peaks have remained almost stationary. For samples above 22.6 percent silicon it was not possible to resolve the $E_0' + \Delta_0'$ structure. Listed in Table I are the energies of the various structures for the thirteen alloys we have investigated together with the positions of these peaks for germanium and silicon as obtained from References [13] and [14]. Plotted in Figure 4 are these energies as a function of silicon concentration. The solid lines represent a linear least square fit of the data in Table I.

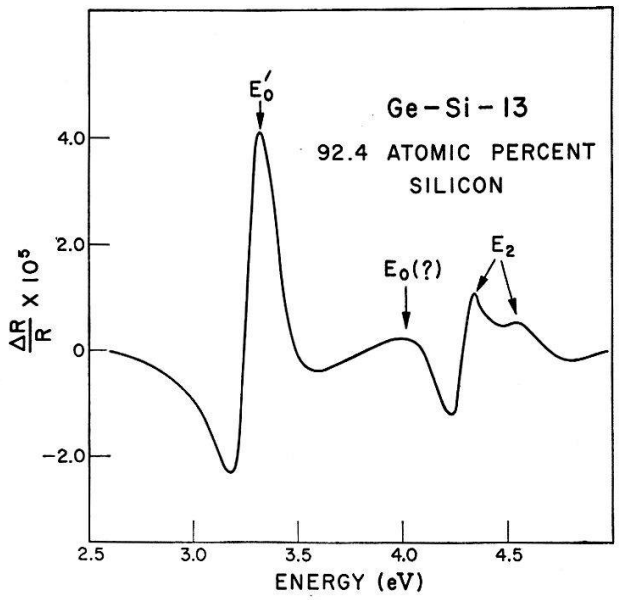

Figure 5

Electroreflectance spectrum of sample Ge-Si-13 at room temperature.

Shown in Figure 5 is the electroreflectance spectrum of sample Ge-Si-13 (92.4 percent silicon), which is very similar to that of pure silicon. Only one structure, E_0', is seen at energies below 3.5 eV. As shown in Figure 4 this peak actually corresponds to a superposition of the E_1 and E_0' doublets of germanium. The structure at about 4 eV, marked E_0 (?), corresponds to the extrapolation of the E_0, $E_0 + \Delta_0$ doublet to this silicon concentration. The E_2 peak exhibits two components (4.34 eV and 4.55 eV) which have also been observed in the electroreflectance spectrum of pure silicon [14]. In reflectivity data two components can also be seen barely resolved at 4.3 eV and 4.5 eV [15].

IV. Discussion

The main features of the concentration dependence of the electroreflectance structures we have investigated are (1) the linear variation of the energies of the peaks, (2) the large concentration dependence of the E_0 and E_1 doublets and the small concentration dependence of E_0' and E_2, (3) the decrease of Δ_0 and Δ_1 with increasing amounts of silicon and (4) the merging of the E_1 and E_0' doublets of germanium into the E_0' structure of silicon.

The concentration dependence of the E_0 and E_1 doublets can be understood by examining the behavior of the Γ_2' level (see Figs. 2 and 6). As silicon is added to ger-

manium this level rises causing an increase in energy of the E_0 doublet. In addition, since the $L_1 - \Lambda_1$ conduction band line is attached to Γ_2' it also rises causing an increase in energy of the E_1 doublet. The decrease of Δ_0 and Δ_1 is due to the smaller spin-orbit splitting of silicon ($\Delta_0 = 0.044$ eV [29]) as compared to germanium ($\Delta_0 = 0.282$ eV [13]). Extrapolation of E_0 to 100 percent silicon indicates that the Γ_2' level is at 4.00 ± 0.05 eV in this material. The addition of a possible quadratic term [24] in the concentration dependence would make this value somewhat higher. In Table II we have listed the values of E_0, $E_0 + \Delta_0$, E_1 and $E_1 + \Delta_1$ extrapolated to pure silicon.

Table II

Energies (in eV) of the E_0, $E_0+\Delta_0$, E_1 and $E_1+\Delta_1$ structures extrapolated to pure silicon.

E_0	$E_0+\Delta_0$	E_1	$E_1+\Delta_1$
4.00 ± 0.05	3.92 ± 0.07	3.37 ± 0.05	3.31 ± 0.05

At a certain silicon concentration the Γ_2' level crosses the nearly stationary Γ_{15} conduction band level (see Figs. 2 and 6). In the region near Γ the Λ_1 conduction band becomes attached to Γ_{15} and rises no higher. However, away from $k = 0$ there is a large admixture of Γ_2' into the $\Lambda_1 - L_1$ band and hence it continues to rise smoothly even after the cross-over has occurred. The admixture of Γ_2' and Γ_{15} into Λ_1, as a function of $\boldsymbol{k}$, for germanium and silicon has been determined from a full zone $\boldsymbol{k} \cdot \boldsymbol{p}$ band calculation [17]. The linear variation of the E_1 doublet indicates that it is the region away from Γ that is responsible for this structure in the alloys and possibly also contributes to the E_0' structure of silicon. Band structure calculations for this material [17, 21, 23, 30] (see Fig. 6) reveal that the Λ_3 valence band and Λ_1 conduction band are nearly parallel, with an energy separation of about 3.4 eV, over a large region of the zone away from Γ. Theoretical optical constants calculations [21, 23, 30] also indicate that this region contributes to the E_0' peak of silicon.

The origin of the 3.4 eV structure in the reflectivity and electroreflectance spectra of silicon has been the source of considerable controversy. According to one viewpoint

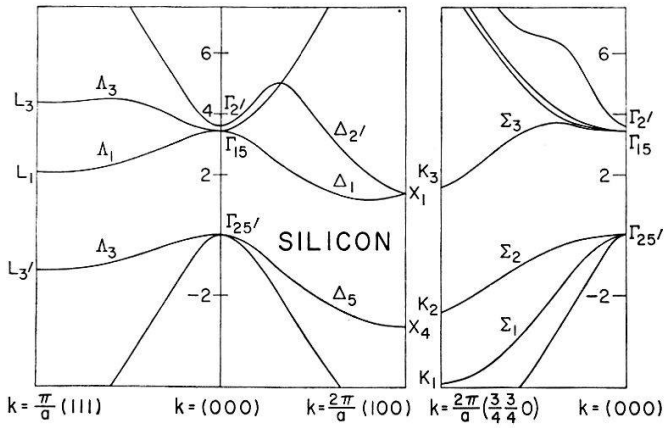

Figure 6

Band structure of silicon as obtained by the $\boldsymbol{k} \cdot \boldsymbol{p}$ method (see Reference [17]). The small spin-orbit splittings ($\Delta_0 = 0.044$ eV) have been neglected.

this peak is caused by $\Delta_5 - \Delta_1$ transitions near Γ. The main experimental arguments given for this assignment are the break in the curve of the E_1 reflectivity doublet as a function of silicon concentration [3] (shown in Fig. 7), d.c. [20] and a.c. [31] piezoreflectivity, and certain electroreflectance [32] experiments. The discontinuity in the TA curve at about 79 percent silicon has been interpreted as a change in the conduction band structure near Γ induced by the cross-over of Γ_2' and Γ_{15}, i.e. the E_0' silicon peak is associated with $\Gamma_{25}' - \Gamma_{15}$ (or nearby $\Delta_5 - \Delta_1$) transitions. No indication of such a break is evident in the data shown in Figure 4. We believe that the greater resolution of the electroreflectance technique as compared to conventional reflectivity yields more accurate results: we have been able to resolve the E_1 doublet up to 54 percent silicon while TA report doublet structure to only 34 percent (see Fig. 7). We have noted that if $E_1 + \Delta_1$ is extrapolated beyond 34 percent is crosses the E_1 curve at about 60 percent silicon. This seems to indicate that there may be some problems of resolution in the work of TA. However, if the average of E_1 and $E_1 + \Delta_1$ is plotted, taking the point at 55 percent in Figure 7 to represent an average, there is much better agreement between our results and those of TA. In addition, the work of SCHMIDT (see Fig. 7) shows that the E_0' and E_1 reflectivity peaks merge at 79 percent silicon. The piezoreflectivity work of GERHARDT [20] strongly suggests Δ symmetry.

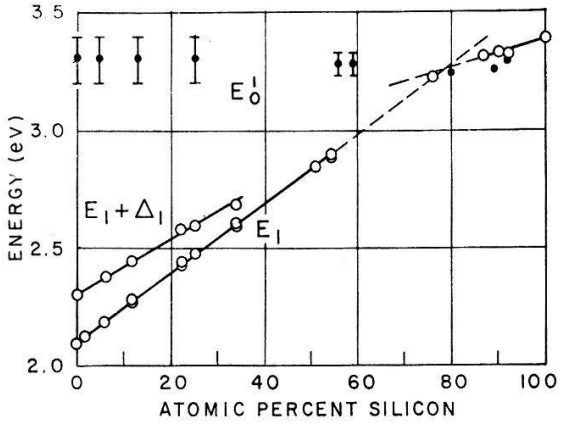

Figure 7

Composition dependence of the E_1 and $E_1+\Delta_1$ reflectivity peaks as measured by TAUC and ABRAHAM (open circles) and the E_0' reflectivity peak as measured by SCHMIDT (closed circles).

Some doubts concerning only a Δ assignment have been raised by several theoretical and experimental investigations. GOROFF and KLEINMAN's [33] pseudopotential calculations of the deformation potentials of silicon yields a value for the pressure coefficient along Δ which is in serious disagreement with the experimental value. They have suggested that E_0' might be due to the $L_3' - L_1$ (or $\Lambda_3 - \Lambda_1$) transitions, for which the agreement was considerably better. HERMAN et al. [22] have calculated $\Gamma_{25}' - \Gamma_{15} = 2.8$ eV for silicon, rather than 3.4 eV, and also find results similar to those of GOROFF and KLEINMAN for the pressure coefficient. The work of both HERMAN et al. and KANE [30] indicate that an extended region of the zone is responsible for this structure, including regions near the Λ axes. DRESSELHAUS and DRESSELHAUS [23] ($\Gamma_{25}' - \Gamma_{15} = 2.43$ eV)

find critical points along Λ, between $k = (\pi/a)$ (0.6, 0.6, 0.6) and L, with an energy separation of about 3.2 eV but report no $\Delta_5 - \Delta_1$ critical points. The silicon band structure shown in Figure 6 has critical points at Δ near Γ and along Λ with a gap of about 3.4 eV. In the calculations of HERMAN et al. and DRESSELHAUS and DRESSELHAUS a critical point at Δ would probably result if the $\Gamma'_{25} - \Gamma_{15}$ gap were raised to a value of about 3.4 eV.

SERAPHIN and BOTTKA [7] have investigated the temperature dependence of the 3.4 eV structure in the electroreflectance of silicon. At room temperature they observe a doublet for this structure while at low temperatures (95 °K to 215 °K) a third peak appears. PHILLIPS and SERAPHIN [7] have interpreted this experiment in terms of a superposition of Λ and Δ transitions. Recently, the effect of uniaxial stress on the E'_0 electroreflectance structure has been studied [19]. Although the gross features of the stress dependence seem to indicate Δ symmetry there are a number of details which are not accounted for on this basis, even taking into account the intraband splitting of the Δ_5 valence band. This may be an indication that transitions other than Δ are involved.

The concentration dependence of E'_0 and E_2 can be explained by examining the bands of germanium and silicon along [100] and [110]. A comparison of Figures 2 and 6 shows that the $\Gamma'_{25} - \Delta_5 - X_4 - K_2$ valence band line and the $\Gamma'_{25} - \Delta_1 - X_1 - K_3$ conduction band line are almost stationary. Therefore, a small variation of the E'_0 ($\Delta_5 - \Delta_1$) and E_2 ($X_4 - X_1$, $K_2 - K_3$) structures is to be expected.

The E_2 peak of sample Ge-Si-13 and pure silicon exhibits two components with a separation of about 0.2 eV. These two components are likely to be the M_1 ($X_4 - X_1$) and M_2 ($K_2 - K_3$ or $\Sigma_2 - \Sigma_3$) singularities required to produce the strong peak observed in the reflection spectrum [34].

V. Acknowledgments

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Anhysteretic Behavior of Evaporated Uniaxial 19Fe 81Ni Thin Films

by **E. Kneller** and **K. Carl**

Ruhr Universität, Bochum, and Max Planck Institut für Metallforschung, Stuttgart, Germany

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Abstract. AC field anhysteretic magnetization $M_a(H)$ and remanence $M_{ar}(H)$ were measured at 20 °C on flat uniaxial 19Fe81Ni thin films in directions parallel to the plane of film. The films were evaporated at substrate temperatures between 100° and 400 °C, and in vacua better than 10^{-6} Torr.

The states $M_a(H)$ above the saturation remanence $M_r(\infty)$ are shown to be thermodynamic equilibrium states from which the anisotropy constant K_u may be obtained.

Below $M_r(\infty)$, $M_a(H)$ and $M_{ar}(H)$ are essentially determined by magnetic interaction fields arising from the dynamic domain structures present during the anhysteretic process. The dynamic domain structures are in equilibrium, the static structures at zero fields are not. From these facts a theory of the anhysteretic susceptibilities χ_a, χ_{ar} is derived, and the results are shown to agree well with experiment.