OPTICAL REFLECTIVITY MEASUREMENTS ON ALLOYS BY COMPOSITIONAL MODULATION

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A new modulation technique is described which enhances the structure in the spectral reflectivity of metals and alloys. This technique allows the determination of the critical energy for optical interband transitions. The method is applied to various α-brass specimens containing between 0.5 and 10 at.% Zn. The threshold energy for interband transitions in these alloys varied between 2.15 and 2.27 eV. The results are compared with those of previous workers obtained by conventional reflectivity measurements.

The understanding of the optical properties of metals, especially the noble metals, was substantially broadened in the early 1960's through the extensive work of Ehrenreich, Philipp, Cooper, and others,[1-7] who successfully interpreted the "structure" in the reflectance and absorption spectra in terms of certain interband transitions. This became possible because at about the same time calculated band structures were published, for example, by Segall,[8] Burdick,[9] and Hanus.[10]

On the other hand, the optical properties proved to be a very useful tool to check and possibly correct the calculated band structures. Recently, interest in optical investigations arose again particularly because of the development of modulation techniques devised to enhance structure in the spectral reflectivity associated with critical points in the joint density of states.[11] In general the optical properties of a crystal are measured as an external parameter is varied periodically to modulate the band structure. By observing the periodic change in properties, essentially the derivative with respect to the external parameter is obtained.

Engeler *et al.*[12] and Gerhardt[13] varied an external stress on solids in different crystallographic directions during reflectance measurements (piezoreflectance). Seraphin and Hess[14] and others studied an electric-field-induced change in the reflectivity of semiconductors (electroreflectance). Berglund[15] and Hanus, Feinleib, and Scouler[16] modulated the temperature during optical absorption measurements. The modulation techniques mentioned above proved to be useful in their specific fields of application. Electroreflectance measurements were predominantly used to study semiconductors, but found little application to metals because it is difficult in this case to maintain large electric fields. Temperature modulation measurements give information in particular about phonon-assisted transitions. Modulation of uniaxial stress provides information on the symmetry of interband transitions. The interpretation of the latter measurements, however, is not simple because the symmetry of a crystal is not preserved when uniaxial stress is applied.

This paper describes another modulation technique, in which the composition of an alloy or the impurity content of a metal is varied. It is anticipated that this method will give additional useful information on the electronic properties of metals and alloys.

Light which comes from a monochromator is split by means of a chopper into two beams so that the two specimens which differ in their composition are illuminated alternately (Fig. 1). The intensity of the light reflected from the samples is measured by a photosensitive device. The ac signal from the photodetector is fed into a lock-in amplifier. A reference signal is picked up from the chopper by means of an auxiliary light source and photocell. The output signal of the lock-in amplifier is proportional to $I_0 \Delta R$. (I_0 contains the intensity of the incident light, the characteristic of the photosensitive device, and other apparatus constants. $\Delta R = R_1 - R_2$, where R_1 and R_2 are the reflectivities of the two specimens. In the case of interest R_1 and R_2 are very nearly equal.) Blocking one of the light beams results in an output signal proportional to $I_0 R_1$ or $I_0 R_2$. The ratio of the two signals provides $\Delta R/R$, i.e., I_0 is eliminated. With this method the light beam is reflected alternately by two samples with composition C_1 and C_2. This is equivalent to the reflection from a sample of composition $(C_1 + C_2)/2$ modulated periodically by a compositional increment $\pm\Delta C/2 = (C_2 - C_1)/2$. A detailed description of the apparatus and experimental technique will be presented elsewhere.

If the major effect of the compositional change is a variation of a critical energy, then enhancement of the structure near critical points is expected. This may be seen by considering the equation

$$\Delta\epsilon_i(\omega) \propto \frac{d\epsilon_i(\omega)}{dC} = \frac{dE_{\mathrm{cr}}}{dC}\frac{d\epsilon_i(\omega)}{dE_{\mathrm{cr}}}, \tag{1}$$

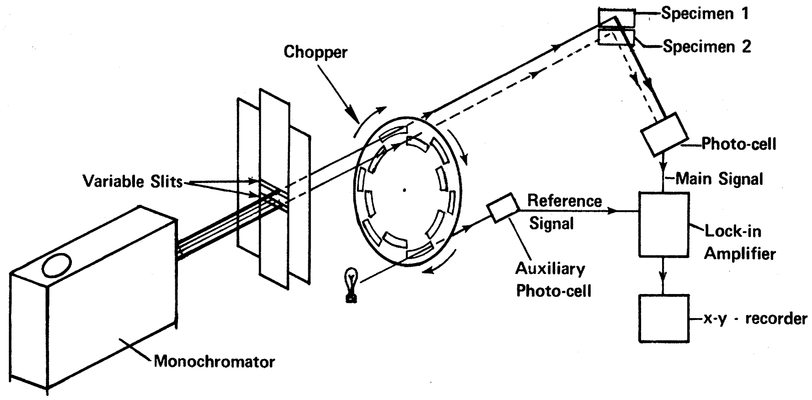

FIG. 1. Schematic diagram of apparatus for measuring $\Delta R/R$ with the modulation technique described in the text.

where ϵ_i is the imaginary part of the complex dielectric constant (which is directly related to R) and $E_{\rm cr}$ is the critical energy for optical interband transitions. The compositional difference between the two samples, ΔC, is assumed to be small and constant. The first factor on the right-hand side of Eq. (1) is independent of ω and is a constant for a particular material and transition. With increasing photon energy $\hbar\omega$, the second term is expected to peak at $E_{\rm cr}$ since ϵ_i usually exhibits a singularity at this energy.[17]

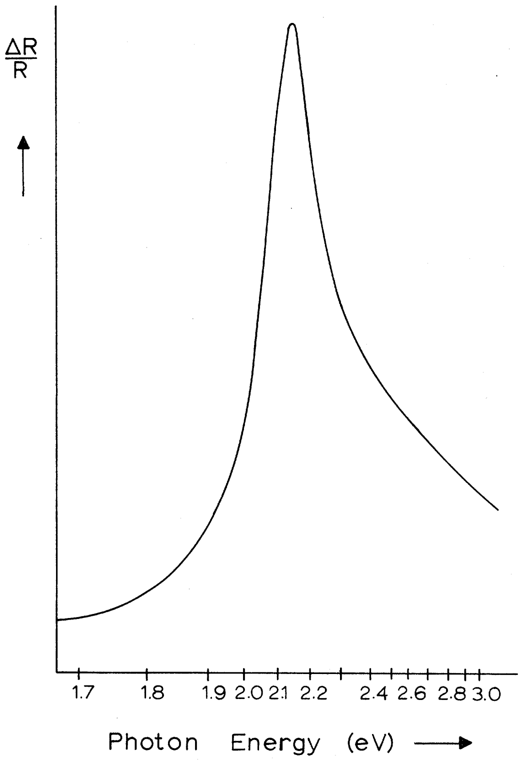

FIG. 2. $\Delta R/R$ (in arbitrary units) versus photon energy of a composite sample Cu/Cu-0.5 at.% Zn. The vertical axis has a linear scale.

This technique is not necessarily restricted to modulating the alloy composition but can likewise be used to study variations in the band structure due to long- and short-range order, oxidation, transformations, surface effects, or differences in various crystallographic directions of single crystals. If two identical specimens are employed and one of them is subjected to a higher temperature, to stress, or to an external electric field it should be possible to obtain similar results as obtained by temperature, stress, or electric field modulation. By rotating the exit slit of the monochromator relative to the grating axis, frequency modulation can also be achieved.

The above-mentioned method was applied to various α-brass specimens which were subjected to identical annealing and polishing procedures. (The samples were mechanically polished, heat treated at 600°C for 80 h, and then fine polished immediately before measurement.) In Fig. 2, $\Delta R/R$ for a pair of specimens, one of which consisted of copper (99.999% purity) and the other of α brass with 0.5 at.% Zn, is plotted versus the photon energy. A peak at 2.15 eV can be clearly

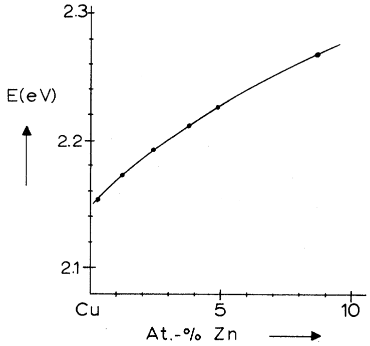

FIG. 3. Maximum photon energies of various Cu-Zn specimens (see Fig. 2).

seen. For specimens with increasing Zn content the photon energy of the peak increases (Fig. 3). This is in agreement with results obtained by Biondi and Rayne[18] and theoretical considerations by Lettington[19] and Amar, Johnson, and Sommers.[20] Investigations using higher photon energies and other materials are in progress.

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SWITCHING AND TEMPERATURE EFFECTS IN LATERAL FILMS OF AMORPHOUS SILICON*

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Self-heating in films of amorphous silicon prior to switching results from application of voltage pulses producing lateral currents. A smooth, rapid, and highly localized temperature rise always precedes the switching event resulting in a filamentary formation bridging the gap. The negative electrode edge is hotter than the positive electrode edge, and the measured filament temperatures compare favorably with temperatures calculated assuming intrinsic conduction takes place in the confined dimensions of the filament channel.

Electrical switching phenomena reported for thin films of amorphous silicon sandwiched between titanium electrodes[1] bears strong similarity to the behavior exhibited[2,3] by mixtures of chalcogenide glassy semiconductors. For silicon it was reported that memory switching is prevalent with ac excitation; a current-voltage characteristic is produced having a high-resistance region linked through a region of negative differential resistance to a low-resistance region. Two conductivity states, high and low, are reported to exist for chalcogenides; transition from one to the other occurs in short time intervals. Upon switching from the low-conductivity state in both the silicon and chalcogenide glass devices, craters or pits in the electrodes are reported which are attributed to filament path formation. For those chalcogenide materals exhibiting memory switching, the ends of filaments are clearly shown[4] by some observers and by others the filaments are displayed from the side.[5] Recent infrared viewer observations[6] on a chalcogenide glass semiconductor reveal a 650-800°C filament during threshold switching.