Optical response of Cu_3Ge thin films

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We report an investigation on the optical properties of Cu_3Ge thin films displaying very high conductivity, with thickness ranging from 200 to 2000 Å, deposited on Ge substrates. Reflectance, transmittance, and ellipsometric spectroscopy measurements were performed at room temperature in the 0.01–6.0, 0.01–0.6, and 1.4–5.0 eV energy range, respectively. The complex dielectric function, the optical conductivity, the energy-loss function, and the effective charge density were obtained over the whole spectral range. The low-energy free-carrier response was well fitted by using the classical Drude–Lorentz dielectric function. A simple two-band model allowed the resulting optical parameters to be interpreted coherently with those previously obtained from transport measurements, hence yielding the densities and the effective masses of electrons and holes. © *1996 American Institute of Physics.* [S0021-8979(96)04710-2]

In the last two decades, the very large integration of microelectronic devices has opened a wide field of research on new low-resistivity materials for interconnections and contacts. Indeed, the scaling down of device sizes requires metals suitable to achieve higher speed and consume less power. Among the investigations on new materials for these purposes, few studies exist on the properties of Cu_3Ge.[1–5]

This compound crystallizes in the monoclinic structure (ϵ phase), with the lattice parameters $a=2.631$ Å, $b=4.200$ Å, $c=4.568$ Å, and $\gamma=89°41'$. Every elementary cell holds a unit formula: the four atoms are randomly placed in $\pm(0,0,1/6)$ and $\pm(1/2,0,1/3)$ sites,[6] so that Cu_3Ge is an intrinsically disordered material.

So far research has been focused on the investigation of transport properties; the most interesting finding is the very high conductivity exhibited by Cu_3Ge thin films, only a factor of 3 lower than that of Cu, and much higher than those of the best known silicides, such as $TiSi_2$ and $CoSi_2$.[1] This makes Cu_3Ge promising in view of possible applications.

Transport measurements have revealed another unusual feature: a marked dependence of the residual resistivity on the thickness of the film, even in the hundreds of nanometers range.[1] This behavior has been ascribed to a strong contribution of surface scattering to electron mobility. Moreover, magnetotransport measurements have shown a positive Hall coefficient and a finite magnetoresistance.[2] On the other hand, there are no published studies on the optical properties or the energy-band structure of Cu_3Ge. In the present work, we investigated the optical properties of Cu_3Ge thin films deposited on Ge, and determined the complex dielectric function $\tilde{\epsilon}(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$, the effective charge density $N_{\mathrm{eff}}(\omega)$, and the energy-loss function $\mathrm{Im}(-1/\tilde{\epsilon})$. We also reexamined all the available experimental data in order to estimate the effective mass and concentration of the free carriers.

Cu_3Ge films were obtained by deposition of a Cu layer on a Ge(111) substrate and by subsequent thermal annealing at 400 °C. The four samples here analyzed, with thicknesses of 200, 500, 1000, and 2000 Å, were the same as in Ref. 2. In the infrared region (0.01–0.6 eV photon energy), normal incidence reflectance and transmittance measurements were performed using a Fourier transform spectrometer Bruker IFS 113v with a resolution of 0.5 meV. From 0.4 to 6 eV the normal-incidence reflectance was measured by a dispersive spectrometer Cary 5. A gold mirror in the infrared region and an aluminum mirror in the visible-ultraviolet region, whose absolute reflectivities were determined independently, were used as references. Ellipsometric spectra from 1.4 to 5 eV were measured at an angle of incidence of 60° using a rotating-polarizer ellipsometer SOPRA ES4G.

Figure 1 shows the reflectance spectra of the different Cu_3Ge samples: they are very similar except for the 200 Å film, which moreover exhibits a nonzero transmittance in the infrared, where the Ge substrate is transparent. Therefore we assumed that the three thickest samples are bulklike, i.e., the measured reflectance coincides with the reflectivity R. This assumption was supported by the direct inversion of the ellipsometry spectra measured at different angles of incidence, which yielded the same dielectric function. On the other hand, effects of interference (due to the multiple internal reflections) and of surface and interface roughnesses make difficult and unreliable the optical analysis of the 200 Å film. For these reasons we will compare the reflectivities of the three thickest samples only.

As one can foresee, R spectra display a metallic behavior, with two characteristic regions. Below about 1 eV, where the intraband transitions (free carriers) dominate, R shows a broad, high-value shoulder (Dingle plateau), approaching unity as the energy decreases to zero. The high-energy limit of such a region is indicated by a rapid fall of R, which reaches a minimum at about 2 eV, roughly corresponding to the energy of the free-carrier plasma resonance, screened by the interband transitions. The shoulder at ≈1.5 eV and the peaks at ≈2.5, 3.0, and 5.3 eV correspond to

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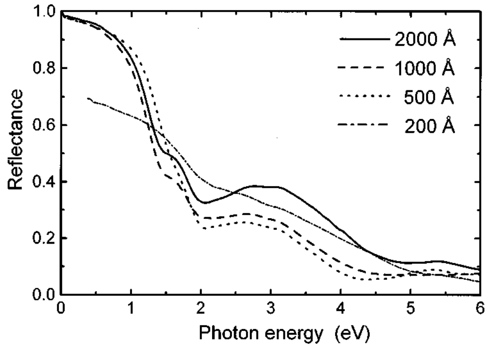

FIG. 1. Reflectance spectra at room temperature and near-normal incidence of the Cu_3Ge films with different thicknesses.

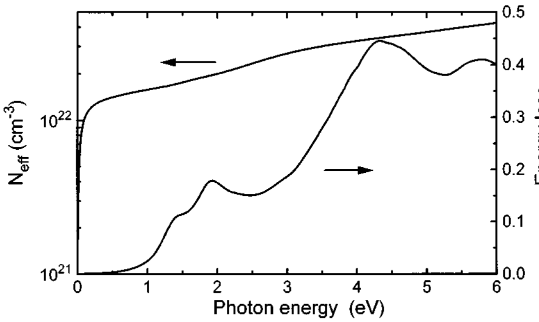

FIG. 3. Energy-loss function $\mathrm{Im}(-1/\tilde{\epsilon})$ and effective charge density $N_{\mathrm{eff}}(\omega)$ of the 2000-Å-thick Cu_3Ge film, derived from optical measurements.

interband transitions. As the thickness of films is reduced, the general trend consists in a broadening and a flattening of the optical structures, while their energy positions remain the same. This is plausible considering that scattering processes become more prominent with the scaling down of thickness, and it is consistent with resistivity measurements showing a similar behavior, ascribed to a strong surface scattering.[2]

The dielectric functions $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ from 1.4 to 5 eV were directly derived by the ellipsometric spectra; outside the ellipsometry range they were obtained through the Kramers–Kronig (KK) analysis of R. To perform the KK transforms, we extrapolated the R spectrum beyond the highest experimental frequency with a power law $R=C\omega^{-p}$, where C and p are positive adjustable parameters. The value of p was chosen so that for some fixed frequencies the resulting dielectric functions match those measured by ellipsometry. Since we are dealing with metallic samples, it is more useful consider the optical conductivity $\sigma_{\mathrm{opt}}=\omega\epsilon_2/4\pi$, which is shown in Fig. 2. Obviously σ_{opt} features and trend reflect those of R.

Then, the effective charge density

$$N_{\mathrm{eff}}(\omega)=\frac{m_0}{2\pi^2e^2}\int_0^{\omega}\omega'\epsilon_2(\omega')d\omega'$$

(m_0 and e are the electron mass and charge, respectively) and the energy-loss function $\mathrm{Im}(-1/\tilde{\epsilon})$ were obtained. For the 2000-Å-thick film, they are illustrated in Fig. 3; the N_{eff} value corresponding to the shoulder in the energy-loss spectrum at ≈1.5 eV, which is due to the screened plasma oscillation of the free carriers, provides an estimate of the free-carriers density.

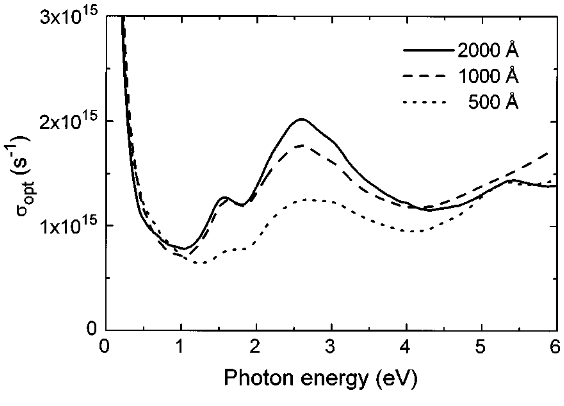

FIG. 2. Optical conductivity $\sigma_{\mathrm{opt}}(\omega)$ of the same Cu_3Ge samples as in Fig. 1.

An evaluation of the differences between the optical response of the films was obtained by best fitting the experimental spectra with a Drude–Lorentz dielectric function:[7]

$$\begin{aligned}\tilde{\epsilon}&=\epsilon_\infty+\tilde{\epsilon}_{\mathrm{fc}}+\tilde{\epsilon}_{\mathrm{bc}}\\&=\epsilon_\infty-\frac{\omega_p^2}{\omega(\omega+i\Gamma)}+\sum_i\frac{f_i}{(\omega^2-\omega_{0i}^2)-i\gamma_i\omega},\end{aligned}\qquad(1)$$

where ϵ_∞ is the high-frequency dielectric constant; $\omega_p=(4\pi Ne^2/m^*)^{1/2}$, N, m^*, and Γ are, in order, the plasma frequency, the density, and the damping parameter of the free carriers, while f_i, ω_{0i}, and γ_i are the oscillator strength, the resonance energy, and the broadening corresponding to the ith interband transition, respectively.

The ω_p value leading to the best fit of experimental data ranges from 4.9 eV for the 2000 Å film to 4.1 eV for the 500-Å-thick film, indicating that N depends only slightly on the thickness. On the other hand, the damping parameter Γ varies strongly, being 0.068, 0.075, and 0.10 eV, respectively for the 2000, 1000, and 500-Å-thick films. This supports the assumption that the dc resistivity dependence on film thickness is mainly due to a different relaxation time $\tau=1/\Gamma$.

Concerning the interband structures, the best-fit parameters show that the width γ_i of the structures at 1.5 and 3 eV increases as the thickness is reduced, while the oscillator strength f_i remains almost constant. On the contrary, the structure at 2.5 eV becomes progressively weaker, maintaining a constant width.

The results obtained on the thickest film were used to estimate N and m^*, and were compared with transport results. In Ref. 2 the transport data were analyzed on the basis of a single-band model, yielding a hole density $p=8.3\times10^{22}$ cm^{-3} and a mean free path $l\approx1200$ Å (assuming $m^*=m_0$). If, on the other hand, this hole density is combined with our plasma frequency, the resulting hole effective mass is $m_h^*\approx6\,m_0$. These values of p, m_h^*, and l are anomalously large ($l\approx400$ Å for pure Cu[6]); furthermore the single-band model does not explain the finite magnetoresistance, which requires the presence of at least two unfilled bands. Therefore we analyzed all the available experimental data in the framework of a two-band model. We recall that the Hall density n_{Hall}, the magnetoresistance $\Delta\rho/\rho$, and the plasma frequency ω_p are functions of the masses of free electrons and holes (m_e^* and m_h^*) and of their densities (n and p) through:[9]

$$\frac{1}{n_{\mathrm{Hall}}}=\frac{p/(m_h^*)^2-n/(m_e^*)^2}{(n/m_e^*+p/m_h^*)^2}, \tag{2a}$$

$$\frac{\Delta\rho}{\rho}=\left[\frac{e^6\sigma_{\mathrm{dc}}^6}{(4\pi\omega_p)^8c^2}\right]\frac{np}{m_e^*m_h^*}\left(\frac{1}{m_e^*}-\frac{1}{m_h^*}\right)^2H^2, \tag{2b}$$

$$\frac{\omega_p^2}{4\pi e^2}=\frac{n}{m_e^*}+\frac{p}{m_h^*}. \tag{2c}$$

The determination of n, p, m_e^*, and m_h^* requires an additional relation, which can be obtained by a rough estimate of the number of the free charges in the primitive cell. Starting from the hypothesis that the Fermi level crosses both the $3s$ Cu band (three times degenerate) and the $2p-2s$ Ge hybrid band, it is clear that, however, the seven valence electrons are arranged in the two bands, a balance between holes and electrons cannot be achieved. So their densities were evaluated in the case of a one hole excess per unit cell, i.e., $p=n+d$, where d is the density corresponding to one carrier per formula unit. Thus, we got $n=2.4\times10^{20}$ cm^{-3}, $p=2.0\times10^{22}$ cm^{-3}, $m_e^*=0.2m_0$, and $m_h^*=1.3m_0$. It is interesting to notice the small density of light free electrons, that plays an important role in providing a high Hall density and a finite magnetoresistance. Assuming that the scattering time $\tau=4\pi/(\omega_p^2\rho_{\mathrm{dc}})$ is the same for electrons and holes, from the previous results we obtained a Fermi velocity $v_F=(\hbar/m_p^*)\times(3\pi^2p)^{1/3}=1.3\times10^8$ cm/s and a mean free path $l=430$ Å for holes, and $v_F=0.8\times10^8$ cm/s and $l=260$ Å for electrons. These values, within the experimental uncertainty, appear to be more reasonable than the corresponding values reported in Ref. 2 and in closer agreement with all other properties of $\mathrm{Cu_3Ge}$.

After some months of air exposure, further measurements showed a decrease in reflectance (≈0.1) and an increase in transmittance (≈0.04) in the infrared spectral range as well as a change in the ellipsometric spectra of the $\mathrm{Cu_3Ge}$ films. An attempt was made to explain these changes by taking into account the growth of a CuO surface overlayer or the surface roughness, modeled by a mixture of $\mathrm{Cu_3Ge}$ with Ge and voids. The fits obtained were poor. On the contrary, the ellipsometric spectra were well fitted by assuming the presence of a thin Ge overlayer, about 100 Å thick. This excess of Ge at the film surface can be ascribed to a diffusion of Cu into the substrate. The causes for such a surface deterioration, probably responsible for the different optical properties of the thinnest film, are under study.

In conclusion, we analyzed the optical properties of $\mathrm{Cu_3Ge}$ thin films from 0.01 to 6 eV. We interpreted both optical data and previous transport results within a two-band model framework, obtaining an estimate of the masses and densities of the free carriers. We observed a remarkable dependence of the optical functions on the film thickness as well as on sample aging.

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