Materials Science in Semiconductor Processing 11 (2008) 340–343

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Density-functional theory study of Au, Ag and Cu defects in germanium

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ARTICLE INFO

Available online 5 December 2008

PACS:
61.72.Bb
71.55.Ak

Keywords:
Germanium
Defects
Metals
Copper
Silver
Gold
Electrical levels
Diffusion

ABSTRACT

Gold, silver and copper defects in germanium are modeled using density functional theory. The structures and electrical properties of the substitutional metals are calculated in excellent agreement with experiment. Interstitial Au, Ag and Cu are found to be shallow donors, in disagreement with a previous assignment of Cu_i to a hole trap in the lower half of the gap. Substitutional–interstitial metal ($M_i - M_s$) pairs and metal–vacancy pairs ($M_s - V$) are also investigated.

1. Introduction

Metal impurities are introduced in germanium during many of the processing steps that take part in the production of metal-oxide-semiconductor devices [1,2]. Cu, Au and Ag are some of the most important among these. Due to their high diffusivity and solubility at high temperatures, they can be inadvertently introduced by in-diffusion during the polishing procedure or during later processing steps such as gate dielectric deposition. Since these contaminants produce deep levels in the gap [1], they can act as carrier traps, affecting the carrier lifetime and leakage current, and therefore their concentration in the substrates should be kept as low as possible.

Extensive experimental investigations have been carried out in copper, gold and silver using resistivity or Hall effect measurements, DLTS and other techniques, and an excellent review can be found in Ref. [1]. Copper, the best known of the three, resides predominately on the substitutional lattice site, where it acts as a triple acceptor [1]. However, the existence of the interstitial species has also been inferred from irradiation experiments [3], and it is believed to dominate its diffusion [4]. According to the present understanding, the passage from the substitutional to the interstitial site occurs via a dissociative mechanism ($Cu_s \rightarrow V + Cu_i$) [4]. Substitutional Au and Ag are amphoteric, with three acceptor states and a deep donor level close to the conduction band. Although their diffusion mechanism is still under discussion, it is believed to be vacancy assisted [4].

Despite the interest of these contaminants, there is still very little information on their interaction with intrinsic defects, dopants and other impurities. This partially owes to the lack of theoretical calculations, justified by

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doi:10.1016/j.mssp.2008.10.007

the difficulty in treating electrically active defects in germanium using the usual local density-functional theory approach [5]. The present paper aims to contribute to the identification of metal-containing defects by providing information on the structures and electrical levels of substitutional metals (M_s) and the results of their interaction with self-interstitials, vacancies and M_i.

2. Method

Spin-polarized density-functional theory calculations were carried out using the AIMPRO code [6]. A Padé parameterization of the exchange-correlation functional of Perdew–Wang was used and the core electrons were accounted for using the dual space separable pseudopotentials of Hartwigsen et al. [7]. To account for the 3*d* semi-core electrons of Ge, a non-linear core-correction (NLCC) was included [8].

A real-space basis set consisting of Cartesian Gaussian functions was used to expand the Kohn–Sham orbitals as described in Ref. [9]. The metal atoms and the germanium atoms closer to the defect core (87 atoms in the undefective cluster) were treated with a *dddd* basis consisting of $(4,4,4)$ (s,p,d) Gaussian type orbitals; for the atoms in the more remote shells of the clusters, we used a contracted basis (C44G*) basis optimized for bulk germanium [5].

The germanium crystal was modeled by large hydrogen-passivated clusters. Clusters centered on the substitutional site ($Ge_{329}H_{172}$), labeled as C_L, and clusters centered on the tetrahedral interstitial site ($Ge_{338}H_{184}$), labeled as C_T, were both used for comparison. Results given were obtained with the C_L clusters unless otherwise stated. The surface germanium atoms and their hydrogen terminators were kept fixed, and all the other atoms were allowed to move during structural optimizations. Saddle points were calculated using the nudged elastic band method [10].

3. Results

3.1. Substitutional metals (M_s)

Substitutional Au, Ag and Cu can be described by the Watkins vacancy model. Accordingly, fully occupied metallic *d* states lie deep in the valence band, whereas metallic *s* states resonate within the conduction band, donating its electrons to the vacancy triplet (t_2) acceptor state. Thus, the electronic structure of a substitutional metal M_s^q in charge state q is similar to that of V^{q-1}, and as for the vacancy, metals with partially filled t_2 states are sensitive to Jahn–Teller distortions. However, it was found previously that these distortions are small when compared to those in silicon [11,12]. The associated Jahn–Teller energies are less than 50 meV, having a minor impact on the calculated electric levels.

There are several ways to estimate electrical levels of defects within the gap. Here we calculate these by comparing electron affinities and ionization energies of the metal under scrutiny with the same quantities obtained for a well characterized center (referred as marker defect), see Ref. [9]. The electrical levels of Au_s, Ag_s and Cu_s have already been determined experimentally, and Au_s, which has well known donor and acceptor levels, will be used throughout this study as a marker to calculate levels of the other defects [9].

Table 1
Calculated electric levels (eV) for Ag_s and Cu_s, using Au_s as marker (top) and substitutional–interstitial metal pairs (bottom).

M_s	$E(0/+)$ $-E_v$	$E(-/0)$ $-E_v$	E_c- $E(=/-)$	E_c $E(\equiv/=)$
Au_s	Marker	Marker	Marker	Marker
	[0.044]	[0.135]	[0.215]	[0.056]
Ag_s	0.01	0.08	0.27	0.11
	[0.035]	[0.116]	[0.302]	[0.144]
			(0.261)	(0.113)
Cu_s	No level	−0.06	0.44	0.28
	No level	[0.037]	[0.42][a]	[0.259]
	No level	(0.0413)	(0.41)[b]	

DLTS energy levels and enthalpy changes ΔH taken from Ref. [1] are given in square and round brackets, respectively.
[a] Measured relative to the valence band: $E_c - 0.322$ eV.
[b] Measured for holes: 0.333 eV.

We thus start by calculating the donor and acceptor levels of Ag_s and Cu_s by comparing their ionization energies, calculated by first-principles, with that of Au_s. The results, shown in Table 1, are in very good agreement with experiment. As expected, the acceptor levels become deeper as the ionic size of the impurity increases, and the absence of a donor level of substitutional copper is confirmed. The first acceptor level of copper is placed slightly below the valence band, but this is still consistent with experiment taking into account that the typical error of the marker method is 0.1–0.2 eV, depending on the proximity between the levels of the marker and of the defect under study.

3.2. Interaction between M_s and vacancies (M_s–V)

The interaction with vacancies leads to the formation of M_s–V pairs with distinct structures depending on the metal. In the Cu_s–V complex, Cu_s resides near to the perfect substitutional site, and is aligned with V along the ⟨111⟩. Despite the contribution of the Cu *d* orbitals to the bonding, the Cu_s–V complex can be regarded as a perturbed divacancy, with an additional electron donated by the *s* orbital of Cu. Thus $\{Cu_s-V\}^-$ has a completely filled doublet ($e^{\uparrow\downarrow\uparrow\downarrow}$) arising from the e_u orbital of the undistorted divacancy (V_2^{2-}), and therefore is not sensitive to Jahn–Teller distortion. In $\{Cu_s-V\}^0$ and $\{Cu_s-V\}^{2-}$ on the other hand, the doublets are partially filled and the C_{3v} symmetry is lowered to C_{1h}. The subsequent electronic configurations, respectively, $\{a'\}^{\uparrow\downarrow}\{a''\}^{\uparrow}$ and $\{a'\}^{\uparrow\downarrow}\{a''\}^{\uparrow\downarrow}\{a'\}^{\uparrow}$, can be viewed as a perturbed $b_u^{\uparrow\downarrow}a_u^{\uparrow}$ and $b_u^{\uparrow\downarrow}a_u^{\uparrow\downarrow}a_g^{\uparrow}$ electronic configurations of the weak-pairing divacancy (V_2^- and V_2^{3-}). The highest occupied a'' and a' electron orbitals of $\{Cu_s-V\}^{2-}$ are, respectively, anti-bonding and bonding [Fig. 1(a) and (b)]. These states, resulting from a hybridization between the V_2 a_u and a_g states and the *d* orbitals of Cu_s, give rise to a $(2-/-)$ level at $E_c - 0.28$ eV