

Formation of Electronic Localized States in Solids Bombarded by Low Energy Particles

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The electronic band structure of Al and Si in the region temporarily collisionally perturbed by impact of low energy particles was calculated using the large-unit-cell pseudopotential method. Kinetic energies in collisions were assumed to be far below the core excitation threshold. The results of the calculation show that localized levels are transiently formed in the perturbed region with energies up to several electronvolts below the valence bands. Electronic excitations of these levels can significantly influence electron and ion emissions from bombarded solids.

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Physical processes of electron and ion emission from solids during bombardment with low energy (< 1 keV) atomic particles are not yet understood in full detail. Electron excitation and subsequent electron emission from bombarded solids are usually explained in terms of four mechanisms. First, there is the classical valence-electron-atomic-particle collision process which is largely responsible for electronic energy losses of the moving particle and which yields a high density of low energy excitations around the Fermi level [1]. Another well documented mechanism is the electron promotion from core levels in a quasimolecule formed transiently during an atomic collision in a solid. This so-called Fano-Lichten process [2] occurs above a certain collisional kinetic energy threshold and leads to creation of electron holes in substrate particles or in the projectile. Subsequent filling of these holes by Auger processes results in high energy electron excitation and emission. When the quasimolecule is formed in front of the surface, electrons from the substrate can fill the "demoted" upper atomic levels. As a result autoionized states are formed which can be also a source of energetic electrons. Finally, electrons are often emitted by projectile neutralization processes [3]. This so-called potential emission, can be experimentally separated [4] and is well understood.

Regarding the ion emission the experimental data have often been interpreted using tunneling and the bond breaking models [5]. Both models are theoretically well justified and are essentially based on the concept of a rapid disruption of secondary particle-surface electronic bonds. The disruption, due to its nonadiabaticity, leads to the particle ionization. Besides these two models, autoionization of excited atoms has been sometimes considered as a possible ionization mechanism. Moreover, when emitted particles contain core level holes, multiply charged secondary ions can be formed [6].

In all the above mentioned models, ion and electron emissions are caused by simple electron-atom or atom-atom collisions in an otherwise unperturbed solid—the existence of the solid is accounted for only through its Fermi level. However, during the particle bombardment the solid is strongly perturbed and a collision cascade is

formed around the impact point of the bombarding particle. Thus a more complex description which would take into account spatial and temporal developments of electronic excitations in the collision cascade should also be considered in the theories of ion and electron emissions. It is quite conceivable that in narrow valence bands of materials such as alkali halides or in core levels of metals and semiconductors, holes (or two holes) could be created at the beginning of the cascade and then transferred to slower secondary particles which are emitted at the later stage of the cascade. This is indeed in agreement with the well known experimental observation that most secondary ions and excited particles have very low kinetic energies. The assumption of long living excitations in collision cascades is generally acceptable for narrow valence bands of insulators or for core levels. On the other hand, in metals and semiconductors bombarded at energies below the core-hole excitation threshold the electronic excitations in valence bands have usually been completely disregarded on the ground that the excitations would dissipate rapidly (within the inverse value of the valence bandwidth, i.e., $\approx 10^{-17}$ sec) compared to the lifetime of collision cascades ($\approx 10^{-13}$ sec). However, in the experiments on ion emission from semiconductors the formation of positive secondary ions (particularly those ions with high ionization energies) is difficult to explain without including substrate excitation [7]. Also recent measurements [8] on electron emission from metals below the core level threshold seem to indicate that more complex solid state effects should be considered. Attempts have been made to overcome some of the problems by phenomenologically describing the substrate excitation with an effective electron temperature [7,9].

In this paper the question is addressed in what respect the region of the low energy collision cascade in metals and semiconductors could differ from a regular solid to prevent rapid dissipation of valence band excitations and possibly to allow the excitations to interact. For this purpose the electronic band structures of a regular metal (Al) and semiconductor (Si) have been calculated in the large-unit-cell approach using the pseudopotential technique and have been compared with the band structures

of solids temporarily perturbed by collisions. The use of pseudopotentials is justified because we are interested only in low energy collisions where the core shells are not perturbed (below ~ 700 eV for Al and Si). Preliminary calculation has been reported by the author [10] using a limited set of local orbitals in an atomic cluster. In the present calculation a more reliable, well converging plane wave approach is used. In this approach the electronic wave function is expanded in plane waves with reciprocal lattice vector \mathbf{G} :

$$\psi_{\mathbf{k}}^{\mu}(\mathbf{r}) = \sum_{\mathbf{G}} a_{\mathbf{k}}^{\mu}(\mathbf{G}) \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}]. \quad (1)$$

The large unit cell is formed by a cube with the side L equal to 15.19 a.u. for Al (containing 32 Al atoms) and with $L = 20.41$ a.u. for Si (containing 64 Si atoms). The suitable pseudopotentials in real space are given by (in a.u.)

$$V_{\text{Al}}(r) = 4.338 \exp(-0.695r^2) - 3.066 \exp(-0.377r^2), \quad (2)$$

$$V_{\text{Si}}(r) = 4.838 \exp(-0.828r^2) - 3.246 \exp(-0.359r^2). \quad (3)$$

These potentials give correct values of the Friedel sum and of the transport scattering cross section. In the present calculation their Fourier transforms $V(\mathbf{G})$ are used.

When the atoms are arranged regularly in the lattice the calculation reproduces very well the known band structures of Al and Si. In the next step the regular lattices have been perturbed by displacing one of the atoms in simulated collisions as shown in Fig. 1. The head-on collision in Al is marked by a dotted line; the collision when one Al atom hits simultaneously two Al atoms is marked by a full line. In silicon the full line marks the collision when one Si atom hits another Si atom in the same layer and comes close to a Si atom in the layer below. In actual cascades there are still more complex collisional configurations possible (more atoms are colliding simultaneously) but they are less abundant and are not considered here. The electronic structures have been calculated for moving atoms frozen at certain positions, marked by black dots in the figure. For simplicity the others atoms remain at their original sites. Also shown in the figure is the atomic repulsion energy (calculated with the scaled Molière potential [11]) in the displaced configurations. It should be emphasized that such configurations exist in solid only temporarily ($t < 10^{-13}$ sec) during collisions. As seen from the repulsion energies, the collisions in the studied system are very soft, far below the core-hole excitation threshold, and thus only valence electrons are perturbed.

In the calculation the wave function (1) was expanded into 475 plane waves, which correspond to the kinetic energy cutoff $E_1 = 54$ eV for Al and $E_1 = 34$ eV for Si. The resulting band structures for the collisional configurations in Al and Si, together with the band structures of regular

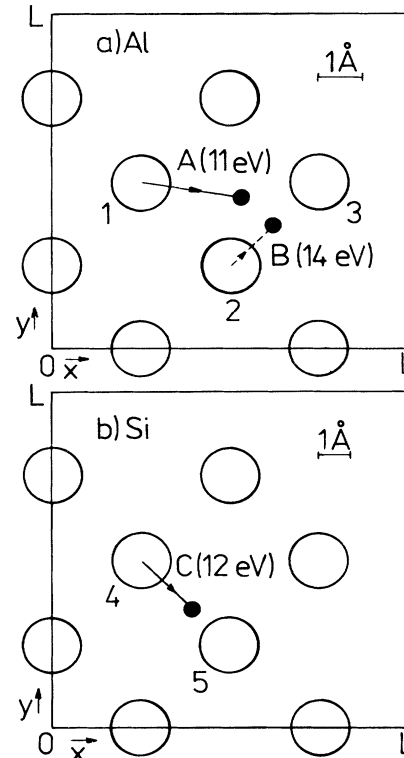


FIG. 1. (a) Atomic configuration in the second (100) layer of the large unit cell of Al. Atoms in their regular positions are shown by circles. In the collision A atom 1 strikes atoms 2 and 3. In the binary collision B atom 1 hits atom 2. The calculations were carried out for frozen configurations in which the moving atoms are stopped at positions marked by black dots. The coordinates (in a.u.) of the frozen atoms are (8.2; 7.1; 3.8) for A and (9.5; 5.72; 3.8) for B . Also shown are the repulsion energies experienced by the displaced atoms. L is the length of the unit cell. (b) Atomic configuration in the third (100) layer of the large unit cell of Si. In the collision C (the only one studied in this paper) atom 4 hits atom 5 and, at the same time, comes close to another Si atom in the layer just below. The coordinates (in a.u.) of the frozen atom are (8.0; 7.3; 4.76).

solids, are shown in Figs. 2 and 3, respectively. Only lower parts of the Al conduction band and of the Si valence band are depicted. It can be seen that well localized states split off the energy continuum in the configuration C in Si and in the configuration A in Al. The localized states have very small dispersion (0.09 eV in Si and 0.26 eV in Al) due to the interaction between unit cells. Small dispersion indicates a strong localization around the colliding atoms. More complex configurations, when four atoms come close together, show even stronger localization. On the other hand, the binary collision B in Al gives rise to a less well defined state which almost merges with the continuum and exhibits a large dispersion (0.7 eV).

It should be noted that with the used kinetic energy cutoff the full convergence was not yet achieved and

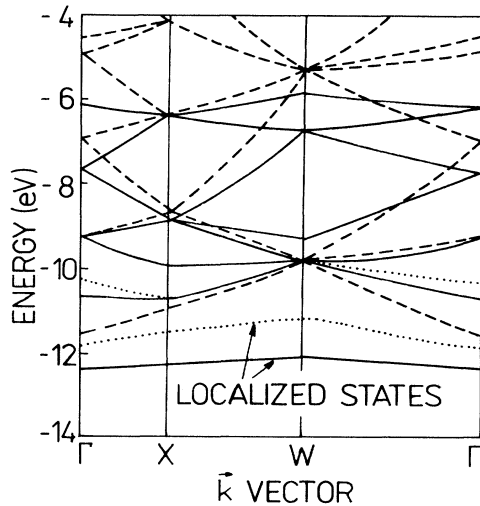


FIG. 2. Energies in the lower part of the Al conduction band calculated the large-unit-cell approach as described in the text. The zero energy is set at the Al Fermi level. The dashed lines correspond to the unperturbed metal, the full lines correspond to the perturbed configuration *A*, and the dotted lines correspond to the configuration *B*. For clarity only a few bands around the bottom of the band are shown for *A* and *B*. The localized states in *A* are quite distinct.

correct energies of localized states in Figs. 2 and 3 are, undoubtedly, still slightly lower. Another approximation is the use of empirical pseudopotentials. Based on the results of the charge distribution calculations the deviation from sphericity of the self-consistent potential is very small. The anticipated variation of a few percent in the spherical part of the pseudopotential would not change the results considerably and thus a fully self-consistent calculation was not carried out.

In real collision cascades several collisional configurations are formed in various parts of the cascade which coincide or overlap in time. Thus the electronic structure of a collision cascade consists of a set of interacting localized levels which, in larger cascades, may possibly form a narrow subband. Once hole excitations are created in these levels the holes, due to their relatively long lifetime, can be shared and possibly transferred to escaping atoms (ionization of secondary particles) or can be neutralized by simple or multiple Auger processes (electron emission) [10]. The holes in the localized states can be created either during the dynamic formation of localized states [10] or more probably, by electron promotions in more energetic target atom-projectile collisions at the beginning of the cascade.

In conclusion, it has been shown that the electron localization in collision cascades is a plausible and a well defined effect which takes place even in broad *s-p* band metals such as Al. The clarification of its precise role in substrate electronic excitations and electron and ion emissions needs, however, further theoretical and experimental investigation. In this respect, studies of kinetic elec-

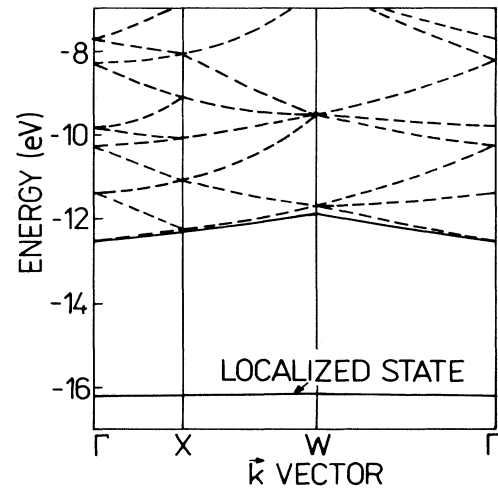


FIG. 3. Energies of the lower part of the Si valence band in the large-unit-cell approach. The zero of energy is set at the top of the valence band. The dashed lines correspond to the unperturbed semiconductor; the full lines correspond to the configuration *C* (only the two lowest bands are shown; the others coincide closely with unperturbed bands). Localization is much stronger than in Al.

tron emission below core level excitation threshold and emission of ions with high ionization energies seem to be of a particular interest. Both processes occur during low energy bombardment of metals and semiconductors and their features are difficult to describe without invoking strong substrate excitation.

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