Ohmic contact formation on n-type Ge

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Abstract

Severe Fermi level pinning at the interface between n-Ge and a metal, leads to the formation of a Schottky barrier, almost independent on the metal work function. Therefore it seems impossible to form metal Ohmic contacts on moderately, n-type doped Ge layers. For p-type Ge the Fermi level pinning works opposite: all metal contacts show Ohmic behavior. This fixed behavior can be altered by the introduction of a thin Ge_3N_4 layer. Ge_3N_4 seems effective in reducing Fermi level pinning and therefore allows the formation of Ohmic contacts on n-type Ge and a rectifying contact on p-type Ge.

Germanium is an important semiconductor material, mainly used in transistors and integrated circuits. A metal-oxide-semiconductor field effect transistor (MOSFET) with Ge channel currently receives much attention as a possible candidate for next-generation high mobility devices, because of the high electron and hole mobility of Ge as compared to Si. However many problems concerning Ge still need to be solved. One problem is the formation of low resistance contacts. Severe Fermi level pinning at the interface between n-Ge and a metal, leads to the formation of a Schottky barrier, almost independent on the metal work function [1]. For Ge n-channel MOSFET devices the lack of low resistance Ohmic contacts leads to high resistance source and drain contacts, limiting the obtainable channel current. The formation of Ohmic contacts on n-type Ge is therefore an important step towards realizing n-MOSFETs in Ge. For p-type Ge the Fermi level pinning works the opposite: all metal contacts show Ohmic behavior. In theory, the fabrication of low resistance contacts on semiconductors is based on selecting a metal with a low work function for n-type semiconductors and a high work function for p-type semiconductors to obtain a low barrier height. In most cases however this method does not work well: interface states pin the Fermi-level and make the barrier height independent of the metal work function. To obtain low resistivity contacts a thin layer of very heavily doped semiconductor is most often used. This leads to a very thin depletion region, known as a tunnel junction, through which field emission can take place. This kind of contacts still requires low barrier heights for high current conduction. For sufficient low barrier heights the formation of a tunnel junction is not needed. Beside good conductivity, Ohmic contacts should also exhibit metallurgical stability. Silicides, stoichiometric compounds of metals and Si, often show these properties and are consequently often used. Germanides, stoichiometric compounds of metals and Ge, are also used on Ge layers. Ti germanide contacts and sulfur-passivated Ni germanide

contacts on n-Ge show barrier height values as low as 0.34 [2] and 0.15 eV [3] respectively, but current-voltage (IV) of these contacts are still clearly rectifying [3].

We investigated the influence of a thin Ge_3N_4 layer, introduced between a metal contact and Ge, on the current conduction. Nitridation of the Ge(001) surface in ultra high vacuum (UHV) by a nitrogen plasma cell is known to form amorphous Ge_3N_4 at temperatures of 100-550°C [4,5]. It was reported that after annealing at 600°C in vacuum this layer completely evaporated, implying that the Ge_3N_4 film is not stable at temperatures above 600°C. Recently we have experimentally shown that exposure of Ge(111) to a nitrogen plasma below 550 °C leads to the formation of an amorphous Ge_3N_4 layer while at a temperature above 600 °C a thin, mono crystalline Ge_3N_4 layer is formed [6]. The Ge_3N_4 formed at high temperature is most likely β-Ge_3N_4 which is the most stable crystalline phase of Ge_3N_4 [7] and has a hexagonal structure. β-Ge_3N_4 can only form an epitaxial layer on three fold symmetric Ge(111). On the Ge(001) plane, the Ge_3N_4 that is formed with high temperature nitridation is in a polycrystalline phase, as we observed by reflection high energy electron diffraction (RHEED). The bandgap of β-Ge_3N_4 has been calculated to be 3.1 eV [7].

The experimental procedure for contact formation is described below. Ge substrates were chemically cleaned to remove metallic contamination, particles and native oxide from the surface, just before loading into an UHV system. Subsequently, annealing in vacuum (~1e-9 Torr) was done to degas the samples. The cleanliness of the surface was confirmed by RHEED, which showed a reconstructed surface. On this clean Ge surface either (poly) crystalline or amorphous Ge_3N_4 was formed by exposure to nitrogen plasma. As reference Ge substrates were prepared in the same way, but without Ge_3N_4 formation on top. Finally, the samples were taken

out of the UHV system and immediately loaded into a metal deposition system to suppress oxide formation. Metal contacts with a diameter of 500 μm were deposited by means of a shadow mask. In order to prevent the metal from reacting with ambient air, an Au capping layer was deposited on top of the metal. As backside contact complete coverage by metal was used. Because of the large surface area, Ohmic behavior could be observed for this contact. We have repeated this experiment for different metals, substrate orientations and doping types. N-type Ge(111) and Ge(001) substrates with a carrier concentration of around 1 x 10^{16} cm^{-3} (~0.15 Ohmcm) were used and also p-type Ge(111) substrates with a carrier concentration of around 2 x 10^{14} cm^{-3} (~15 Ohmcm). X-ray photoelectron spectroscopy measurements revealed the formation of a ~0.7 nm Ge_3N_4 layer in the case of crystalline Ge_3N_4 on Ge(111). No post deposition anneal was performed. IV measurements were performed between the front and backside contacts.

For the Al contact on n-Ge(111) without intermediate Ge_3N_4 a rectifying behavior was observed, as reported by others [1]. The sample with Ge_3N_4 intermediate layer however showed Ohmic behavior with a current density of 14 A/cm^2 at –1 V, as shown in Figure 1. The lack of current saturation in reverse and the obtained current densities indicate the barrier height of the contact is smaller than 0.3 V.

Ni germanide (NiGe) is often used to form low resistance contacts on n-Ge, with reported barrier heights ranging between 0.39 [2] and 0.61[3]. Therefore NiGe/n-Ge(111) contacts were made as a comparison to Al/Ge_3N_4/n-Ge(111) contacts. From Figure 1 and Table I it is clear that the Al/Ge_3N_4/n-Ge(111) contact shows much better current conduction than NiGe/n-Ge(111). The barrier height of the NiGe/n-Ge(111) contact was calculated from the reverse current to be 0.60 eV, close to the value reported by reference 3.

Al contacts with an amorphous intermediate Ge_3N_4 layer showed a comparable current conduction as for Al contacts with a crystalline Ge_3N_4 layer. Therefore it seems that both amorphous as crystalline Ge_3N_4 layers lead to improved current conduction for Al contacts on n-Ge(111).

The influence of an amorphous Ge_3N_4 and a polycrystalline Ge_3N_4 intermediate layer for Al contacts on n-Ge(001) was investigated. For both contacts the IV measurements showed Ohmic behavior. It was necessary to reduce the nitrogen plasma exposure time for the formation of amorphous Ge_3N_4 on Ge(001) in comparison with Ge(111) to obtain similar behavior. This suspects that the Ge_3N_4 thickness is larger in the case of Ge(001) for the same nitrogen plasma settings and exposure time. This can be explained by the denser atomic surface packing of Ge(111) which can limit the rate of Ge_3N_4 formation in respect with Ge(001). This points to the advantage of using high substrate temperatures during plasma nitridation, because this leads to an equilibrium between formation and dissociation of Ge_3N_4. This equilibrium limits the obtainable thickness and therefore allows accurate thickness control [6].

We have also investigated other methods than nitrogen plasma exposure in vacuum to obtain a Ge_3N_4 layer on top of Ge. Annealing in nitrogen and ammonia atmosphere also showed improved contacts for Al.

The current conduction of different metals on n-Ge(111) has been investigated. Al, Cr, Co, Au and Pt contacts were used. All contacts without Ge_3N_4 showed rectifying behavior. The insertion of a thin Ge_3N_4 layer did not change the electrical behavior of the junction for Au and Pt: the IV characteristic remained clearly rectifying. For Al, Cr and Co on the other hand the addition of a thin Ge_3N_4 layer has a large influence on the IV characteristics. For these metals the

junction has become Ohmic: high current density both in forward and reverse bias, see Figure 2. From the reverse currents the barrier height was calculated and summarized in Table II. From the IV behavior of different metal contacts it can be concluded that the introduction of a thin Ge_3N_4 layer clearly reduces the Fermi level pinning, and therefore allows changing the barrier by choosing a metal with different work function.

At the surface of a semiconductor with covalent bonds atoms have unpaired electrons, often referred to as dangling bonds. These dangling bonds can either give up or accept an electron. The corresponding surface states may be situated in the forbidden band gap as is the case for Ge [1]. Depending on the surface states distribution and the Fermi level of the bulk, these states will be partially filled and therefore can lead to a positive or negative net surface charge. The position of the Fermi level at which the surface is electrically neutral is called the charge neutrality level. The large density of surface states of Ge will force the Fermi level to the position of the charge neutrality level, which is situated slightly above the valence band in the case of Ge [1]. An electron depletion region and consequent electron barrier are formed at the n-Ge surface. This barrier still exists when a metal is deposited and is almost independent of the metal work function. Therefore all metal contacts on n-Ge lead to rectifying behaviour. Amorphous Ge_3N_4 has been shown to be a good passivation of Ge(001) [4]. It has also been shown by theoretical calculations that crystalline Ge_3N_4 is a passivation layer for Ge(111) surfaces [7]. A thin Ge_3N_4 layer, regardless whether it is amorphous or crystalline, will reduce the number of dangling bonds at the Ge surface and therefore the surface state density. The difference in Pauling electronegativity of nitrogen and germanium is 1.0. Therefore the Ge-N binding is not pure covalent, but partially ionic. From this polarized covalent binding, the Fermi level pinning is expected to be low [8]. Therefore the Ge_3N_4 has a double effect: (1) it terminates dangling bonds

at the Ge surface states and consequently reduces the trap density at the Ge_3N_4/Ge interface; (2) it contains less surface states, and therefore the metal/Ge_3N_4 interface shows much less Fermi level pinning. Because Ge_3N_4 is a wide band gap semiconductor and therefore acts as a barrier layer for electron injection, this layer should be kept thin enough so that carriers can tunnel easily through it. For p-Ge the Fermi level pinning close to the valence band is beneficial for the formation of a p-type Ohmic contact: even when a metal with work function smaller than the sum of the Ge electron affinity and band gap is deposited, an Ohmic contact is formed. If the model presented above is correct, Ge_3N_4 passivation of p-Ge is expected to allow the formation of Schottky barriers. Indeed we clearly observe rectifying behaviour of Al contacts on p-Ge(111) with a crystalline Ge_3N_4 intermediate layer, see Figure 3. For Cr the difference between the metal work function of Cr (4.5 eV) and the Ge electron affinity (4.1 eV [9]) is 0.4 eV. Hence, a barrier height of 0.4 eV would be expected for an n-Ge/Cr contact in the absence of surface states. When a Ge_3N_4 layer is inserted, the barrier seems to be smaller than 0.3 V. This could indicate the existence of a dipole, at the Ge_3N_4/Ge interface or the metal/Ge_3N_4 interface which changes the barrier height. A dipole at the Ge_3N_4/Ge interface can be explained by the polarized covalent binding between Ge and N.

In summary, we have investigated the influence of thin intermediate Ge_3N_4 on metal contacts on Ge. Different methods can be used to create such a layer, among them nitrogen plasma exposure, anneal in nitrogen and ammonia atmosphere, resulting in amorphous or (poly)crystalline Ge_3N_4. Where rectifying behavior is observed for all metal contacts on n-Ge, the insertion of a thin Ge_3N_4 layer leads to Ohmic behavior for Al, Cr and Co. Contacts on n-Ge of Au and Pt, which have a higher work function than the previously mentioned metals, still show rectifying behavior when a thin Ge_3N_4 layer is inserted. For p-Ge the introduction of a thin

Ge_3N_4 layer can invoke rectifying behavior instead of Ohmic behavior on bare p-Ge. The experimental results have been explained in terms of (1) the passivation of Ge surface states by Ge_3N_4 and (2) the ionic character of the covalent Ge-N binding which limits the number of Ge_3N_4 surface states. As Ge_3N_4 is a wide bandgap semiconductor, this layer should be kept thin enough to allow electrons to tunnel easily through it. A dipole at the Ge_3N_4/Ge interface could have an influence on the barrier height. The high current conduction of metal/Ge_3N_4 contacts on n-Ge makes dopant implantation to form a tunnel junction superfluous. Furthermore this contact is not stretched into the Ge as for germanides and is therefore shallow. In the case of Ge-based field effect transistors Ge_3N_4 might be used for gate passivation [6] and for contact improvement. Therefore only one Ge_3N_4 deposition step is needed to achieve both goals.

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Tables

Table I: Comparison of current density and resistance measured between top and back contact at -1 V and between two top contacts at 0.5 V respectively for different contacts on n-Ge.

Contact	**Current density (A/cm^2)**	**Resistance (Ohm)**
$Al/Ge_3N_4/Ge$	13.9	16
Al/Ge	5.5×10^{-4}	5.3×10^{5}
NiGe/Ge	8.9×10^{-3}	4.3×10^{4}

Table II: Metal work function for different metals from ref. 10 and the barrier height calculated from IV measurements. For Al/Ge_3N_4, Cr/Ge_3N_4 and Co/Ge_3N_4 contacts no barrier was observed and therefore the barrier height is at least smaller than 0.3 eV.

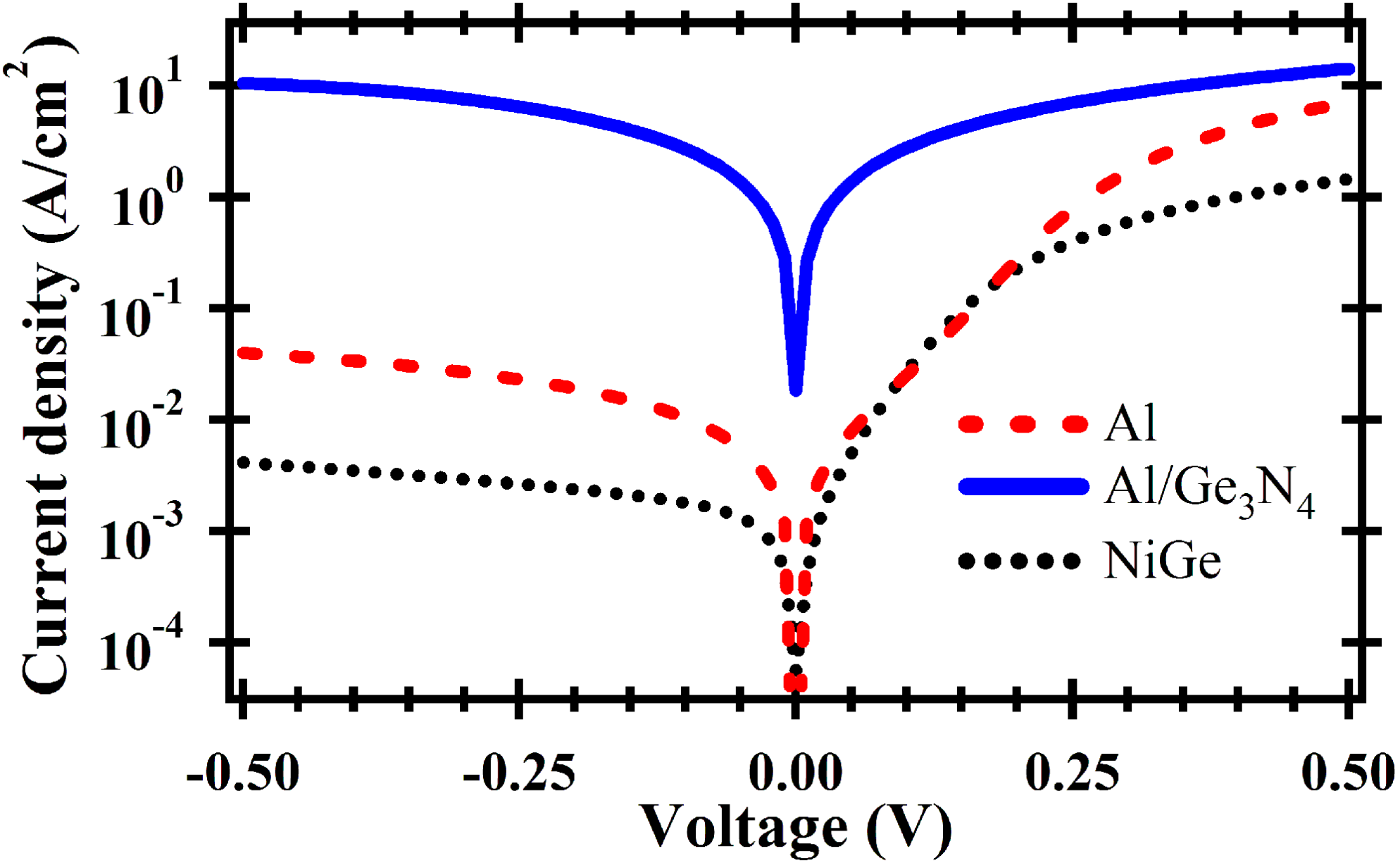
Metal	**Work function (eV)**	**Barrier height (eV)**	
		no Ge_3N_4	**Ge_3N_4**
Al	4.17	0.61	< 0.3
Cr	4.5	0.52	< 0.3
Co	5.0	0.55	< 0.3
Au	5.38	0.59	0.51
Pt	5.64	0.64	0.54

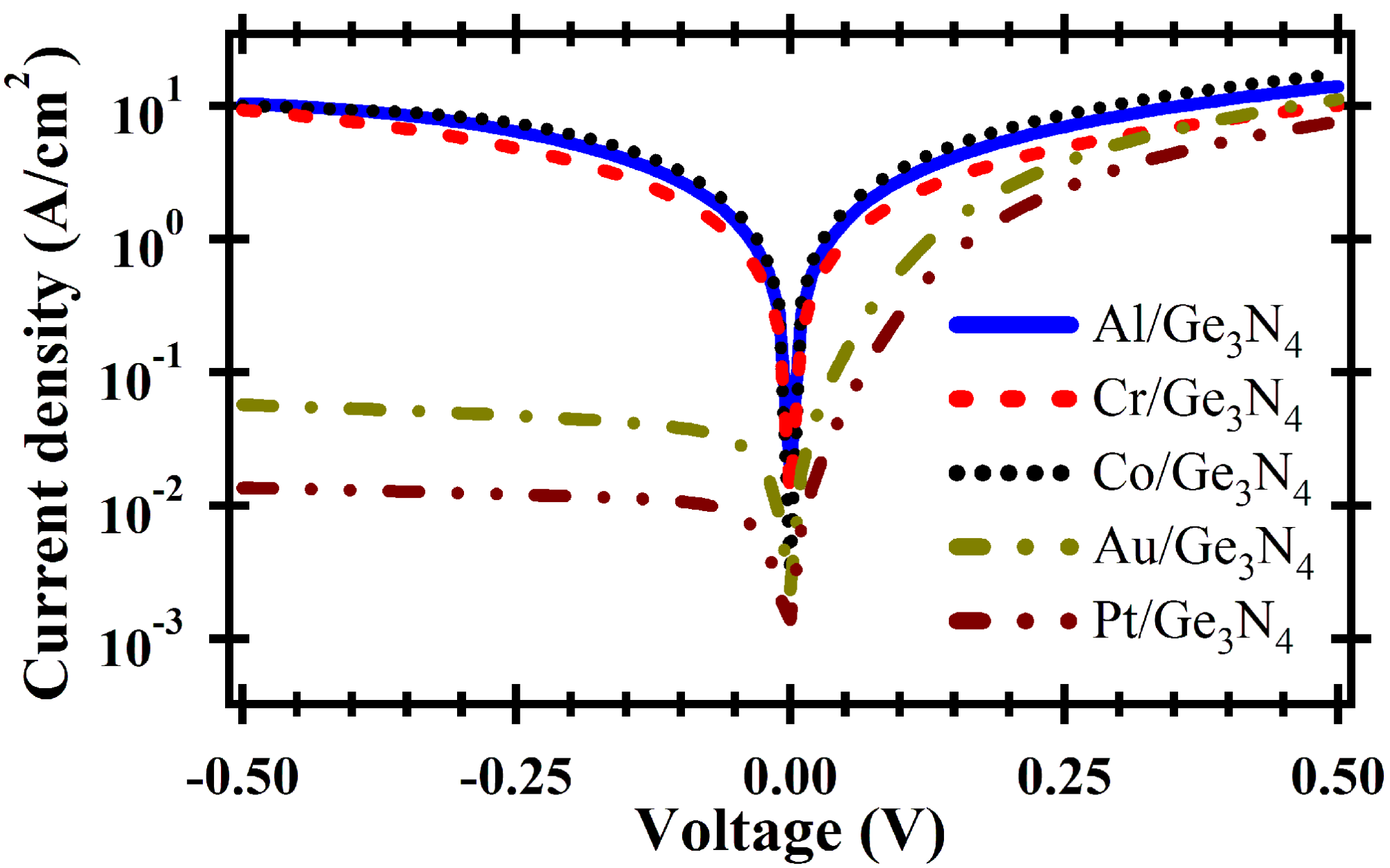
Figure captions

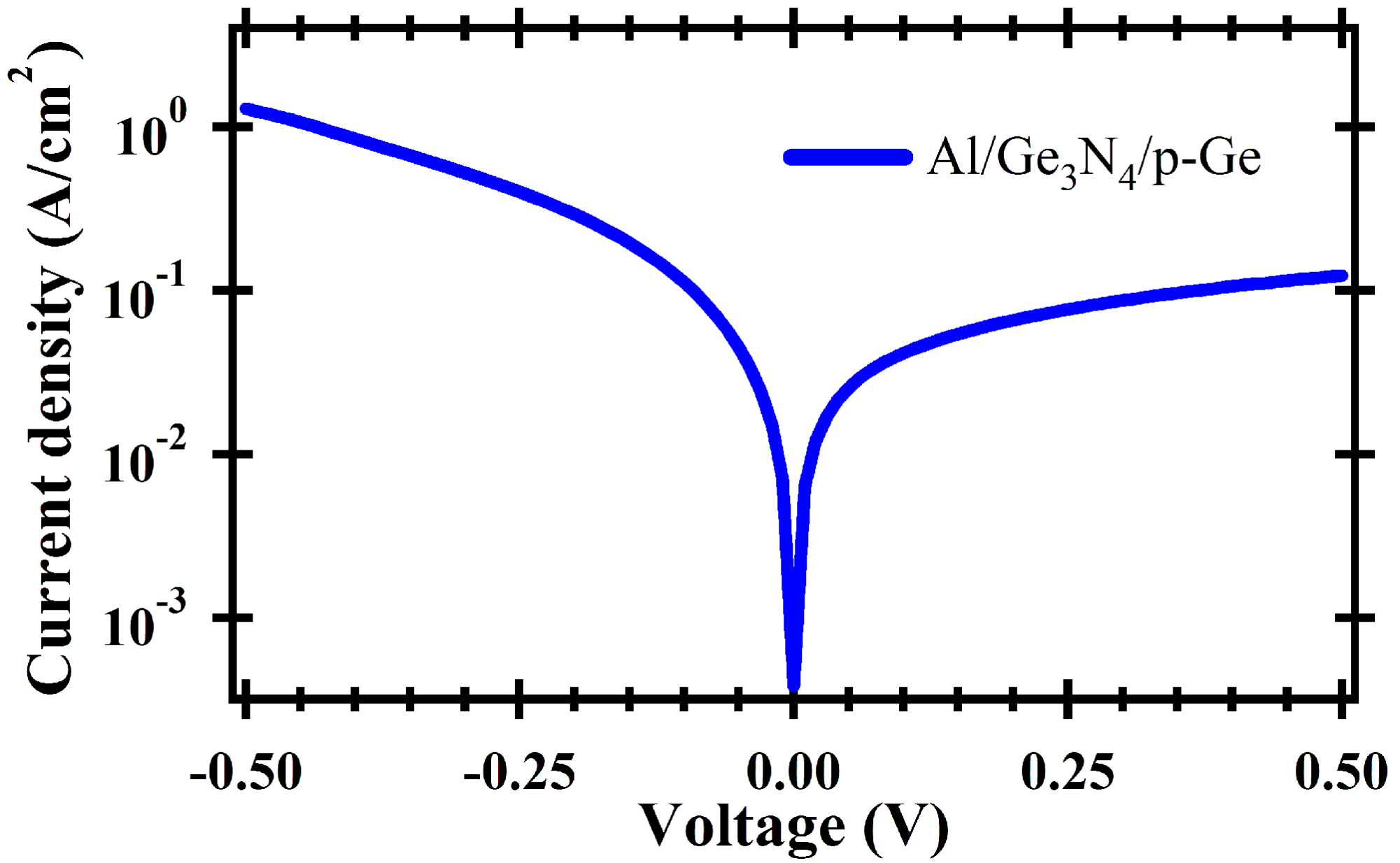
Figure 1: IV measurement between a top and backside Ohmic contact on n-Ge(111). The top contact consists of Al/Ge_3N_4 (solid, blue line), Al (dashed, red line) or NiGe (dotted, black). The insertion of a thin Ge_3N_4 layer clearly changes the contact behavior of Al from Schottky to Ohmic. Al/Ge_3N_4 contacts shows much better current conduction than NiGe.

Figure 2: IV measurement between a top metal/Ge_3N_4 contact and the backside Ohmic contact on n-Ge(111). Solid (blue) line for Al, dashed (red) line for Cr, dotted (black) line for Co, dotted-dashed (green) line for Au and dotted-dotted-dashed (brown) line for Pt. Al, Cr and Co form Ohmic contacts when a Ge_3N_4 layer is inserted. Au and Pt stay rectifying.

Figure 3: IV measurement between a top Al/Ge_3N_4 contact on p-Ge(111) and the backside Ohmic contact. The Al/Ge_3N_4 contact on p-Ge is clearly rectifying.


Current density (A/cm^2)
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
-0.50
-0.25
0.00
0.25
0.50
Voltage (V)
Al
Al/Ge_3N_4
NiGe


Current density (A/cm^2)
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
-0.50
-0.25
0.00
0.25
0.50
Voltage (V)
Al/Ge_3N_4
Cr/Ge_3N_4
Co/Ge_3N_4
Au/Ge_3N_4
Pt/Ge_3N_4


Current density (A/cm^2)
10^0
10^{-1}
10^{-2}
10^{-3}
Al/Ge_3N_4/p-Ge
-0.50
-0.25
0.00
0.25
0.50
Voltage (V)