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Inter-diffusion in compositions for transparent contacts

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Abstract

Contact structures using contact materials Au, Ge and Pd on *n*-type GaAs were metallized, formed and studied. The transfer characteristics, namely contact resistivity (ρ_c), for the structures was assessed using transmission line model. The results showed that the structures under appropriate annealing conditions (period and temperature) exhibit ohmic behaviour with low contact resistivity ρ_c (~10^{-6} Ω cm^2). It was found that ρ_c decreases with increasing annealing temperature up to ~180 ^{0}C. The ρ_c was also found to decrease with increasing substrate-doping density. The contact formation mechanism for the structures Au/Ge/Pd was also studied by a compositional analysis. The compositional distribution in metallization was investigated by collecting the Rutherford 2.3 MeV $^4He^{++}$ backscattering spectra for the as-deposited structures and the structures after annealed. The results supported the Au-Ge inter-diffusion mechanism. However, the factors which were crucially responsible for the Au/Ge/Pd transparent-contacts with low contact resistance are the solid-phase regrowth, inter-diffusion between Au and Ge, and the enhancement of the conductivity of the excess Ge due to the incorporation of Au.

Keywords: Contact resistivity; Annealing; Lithography; Inter-diffusion

1. Introduction

Contact structures with different contact materials and conditions have been studied both theoretically [1,2] and experimentally [3-7] from the point of view of achieving photo-diode [4] and transparent devices. Recent advance in semiconductor technology has made it possible to fabricate high performance GaAs-based devices. However, reliable low-resistance ohmic contacts of small size are very required for future applications in low-dimensional sub-microscopic or nanoscopic devices.

For the ohmic contacts to *n*-GaAs, Au-Ge based materials, such as AuGe/Au, AuGe/Ni and AuGe/Ni/Au have widely been used. For example, the commonly used spiking ohmic contact AuGe/Ni is achieved by alloying an AuGe/Ni multilayer structure at high temperatures, generally higher than the Au-Ge eutectic temperature (361 ^{0}C), for a short period of time [7]. However, this metallization presents several drawbacks mainly due to the problematic control of the alloying liquid phases because the ohmic behaviour of the Au-Ge based contacts is known to be a result of liquid phase reactions. The AuGe/Ni metallization therefore presents several serious disadvantages, such as poor contact edge definition and large spread of the contact resistivity within a single wafer, problems in reproducibility and insufficient contact reliability owing to the presence of the β-AuGe phase (liquid-like flow) of low melting point in a contact with GaAs substrate. This edge spreading could limit the use of the AuGe/Ni contact in GaAs-based submicron devices.

Here, in this investigation, contact structures Au/Ge/Pd on GaAs have been metallized, formed and studied. Substrates with different *n*-doped GaAs are used. The study shows that the structure Au(100 nm)/Ge(40 nm)/Pd(10 nm), annealed at 180 ^{0}C for 1 h, contacts higher *n*-doped GaAs more reliably with low contact resistance. With the aid of the Rutherford backscattering spectrometry, the contact formation mechanism is also discussed in details.

2. Experimental

Substrates used in the present investigation were semi-insulating GaAs (100) wafers with Si-doped surface layers (0.2 nm, ~0.1 kΩ/sq) prepared by metal-organic chemical vapor deposition. For the substrate-doping density dependence, samples with different carrier densities (known from Hall measurements) were used. Prior to contact deposition, the substrates were cleaned using conventional organic solvents. The native surface oxide was then removed using $HCl:H_2O$ (1:1 vol.) followed by a de-ionized water rinse and blown dry with nitrogen before loading the substrates in the evaporation chamber. Au(100 nm)/Ge(40 nm)/Pd (10 nm) contact samples were then deposited on the substrates, with Pd layers adjacent to the GaAs substrates, using an e-beam evaporator with a base pressure of ~5x 10^{-8} Torr. The contact metallization was annealed in a tube furnace in flowing nitrogen at different temperatures to study the annealing temperature dependence. The specific contact resistivity (ρ_c) was measured using transmission line model (TLM) [8]. According to the TLM, the total resistance (R), measured between two contact pad spacing (*d*), is given by [8,9]

$$R = \left(\frac{R_s}{w}\right)d + 2l_T\left(\frac{R_s}{w}\right)\coth\frac{l}{l_T}, \quad (1)$$

where l is the contact length, w is the contact width, l_T is the transfer length and R_s is the sheet resistance. The contact spacing is related to the transfer length as $d = 2(R_c w / R_s) = 2l_T$, where R_c is the contact resistance. As is the present case, if d is much greater than l_T, the effective contact area (A_{eff}) becomes wl_T instead of wd, so the ρ_c (for samples showing linear *I-V* plots) can be found as

$$\rho_c = R_c A_{eff} = R_c w l_T = R_s l_T^2 . \quad (2)$$

When d is much greater than l_T, the $\coth(l / l_T)$ term of Eq. (1) approaches unity so that R_s and l_T can be determined from a plot of R versus d for various contact spacings. The *R-d* plot yields a straight line, where the slope of the line gives the value of R_s/w and the intercept with the R-axis gives the value of $2l_T(R_s / w)$ from which l_T can be evaluated by using the value of R_s/w. Finally, the relation presented in Eq. (2) gives the value of ρ_c.

The contact resistance was measured using two- and four-terminal measurements and a HP4145B parameter analyser to extract *I-V* curves and resistance. In the calculation, we assume that the parasitic prove resistance is accurately known and subtracted from the measurement results. The compositional distribution in metallization was investigated by collecting Rutherford (2.3 MeV $^4He^{++}$) backscattering spectra for the as-deposited structures and the structures after annealed.

3. Results and discussion

Thicknesses of a multilayer required for a reliable contact to *n*-type GaAs have been established in an earlier study [6]. Based on that, contact structures of the type Au(100 nm)/Ge(50 nm)/Pd (10 nm), as shown in Fig. 1, were metallized. In order to find out the better annealing conditions, we study the annealing temperature dependence of the contact structure. Here, the contacts were processed at low temperatures, much lower than the Au-Ge eutectic temperature.

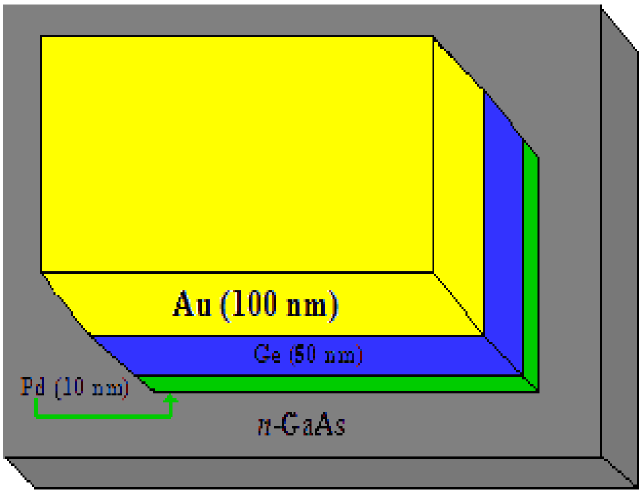

Figure 1. Investigated contact structure Au(100 nm)/Ge(40 nm)/Pd(10 nm). Only one contact pad is shown on the *n*-type GaAs substrate.

Figure 2 shows the contact resistivity ρ_c as a function of annealing temperature (T_a) for the fixed annealing time of 1 h (n_D = 1x10^{18} cm^{-3}). Points show the averages of the experiment data obtained from several experiments. As found, ρ_c first decreases with T_a and then it increases. The minimum value of ρ_c ~10^{-6} Ω cm^2 is obtained at ~180 ^{0}C. It was also found that the same resistance value for a contact structure annealed at comparatively higher T_a can be achieved by annealing it for a comparatively shorter time period. When the contact structure is annealed at T_a~180 °C for 1 h, the reactions begin at the Pd–GaAs interface to form a metastable Pd_4GaAs phase at lower temperature.

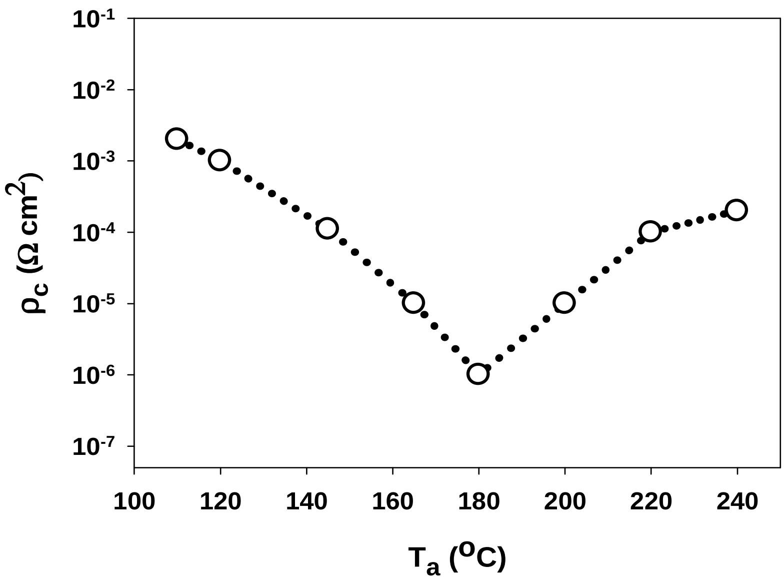

Figure 2. Dependence of ρ_c on the 1-hour annealing temperature for the contact.

However, this ternary phase is decomposed at elevated temperatures, near T_a~180 °C, driven by the excess Ge for the formation of PdGe. This process results in a regrown n^+-GaAs layer doped with Ge, where the excess amorphous Ge remains on top of the PdGe layer because the transport of the excess Ge across the PdGe layer to form an epitaxial Ge layer on the regrown n^+-GaAs layer is not expected at this temperature, and consequently, the conductivity of the excess amorphous Ge is enhanced (as a result of in-diffusion of Au into the excess Ge). Thus, the factors which are crucially responsible for the observed low contact resistance for the contact annealed at 180 °C for 1 h are the solid phase regrowth, inter-diffusion between Au and Ge (Au diffuses into Ge-rich region and *vice versa*) and the enhancement of the conductivity of the excess Ge due to the incorporation of Au. It was also found that the as-deposited contact structure was not ohmic (even non-ohmic after annealed at 130 °C for 1 h). However, the contact Au(100 nm)/Ge(40 nm)/Pd(10 nm) annealed at 180 °C for 1 h displayed good ohmic behaviour with the lowest contact resistivity (ρ_c ~10^{-6} Ω cm^2).

Dependence of contact resistivity on the substrate doping density for different annealing temperatures is shown in Fig. 3. Points are the experimental data and the lines are the least-squares log-log fits to the data. As can be seen, the variation is an inverse relationship for the whole rage of doping density. The experiment was repeated several times. In each experiment, samples of different substrate doping densities underwent pattering, deposition, processing and annealing with the same conditions at the same time in order to allow as much control as possible within the experiment. A least-squares log-log fit to the average of the experimental data was made, which gives the relationship $\rho_c \propto n_D^m$ with m=1/2, where n_D is the substrate doping density. From a theoretic calculation for the AuGe/Ni contacts, Braslau [7] predicted the same type (power) of relationship with m=1. It is worthy to note here that his theories invoked spreading resistance due to laterally inhomogeneous contacts, or a high barrier due to a thick n^+ surface region much greater than the depletion width. In the present case, the resistance of the contacts are most likely not limited by the above reasons because of a naturally low barrier at the Pd/GaAs interface or of an effective lowering of the interfacial barrier due to the creation of a thin n^+ interfacial region, or both. The substrate doping density dependence also agrees with the experimental results for the Pd-In-Ge contacts as well as with the results for the Au-Ge contacts using δ-doped surface layers to n-GaAs [9].

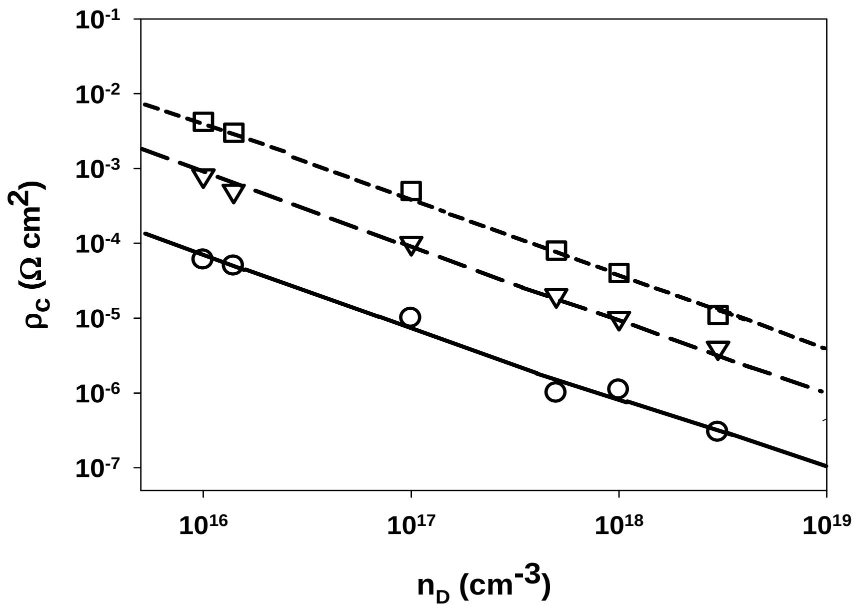

Figure 3. Specific contact resistivity as a function of the substrate doping density for the contact annealed at different temperatures (circles: 180 ^{0}C, down triangle: 160 ^{0}C and square: 220 ^{0}C).

In order to explore the contact formation mechanism rigorously, we now present the results of the Rutherford backscattering spectra. The element composition of the contact as a function of depth can be ascertained from the Rutherford backscattering spectra. Figure 4 shows the Rutherford backscattering spectra for a contact structure Au(100 nm)/Ge(40 nm)/Pd(10 nm) for the as-deposited and the structure after annealed at 180 ^{0}C for 1 h. The individual layers of Au, Pd, and Ge are well spatially confined in the as-deposited sample. However, the spectrum also shows that Pd has slightly reacted with the upper Ge layer and also may have slightly reacted with the GaAs substrate in the as-deposited stage. After annealing at T_a~180 °C for 1h, the Rutherford backscattering spectrum clearly shows the in-diffusion of Au into the Ge layer. The incorporation of Au in the Ge will enhance the conductivity of the Ge. From the Rutherford backscattering spectra, the redistribution of

Ge, after annealing, shows the reaction of Ge with the Au layer. Although the detailed reactions cannot be determined from the Rutherford backscattering spectra, Fig. 4 supports the Au–Ge inter-diffusion model for the contact.

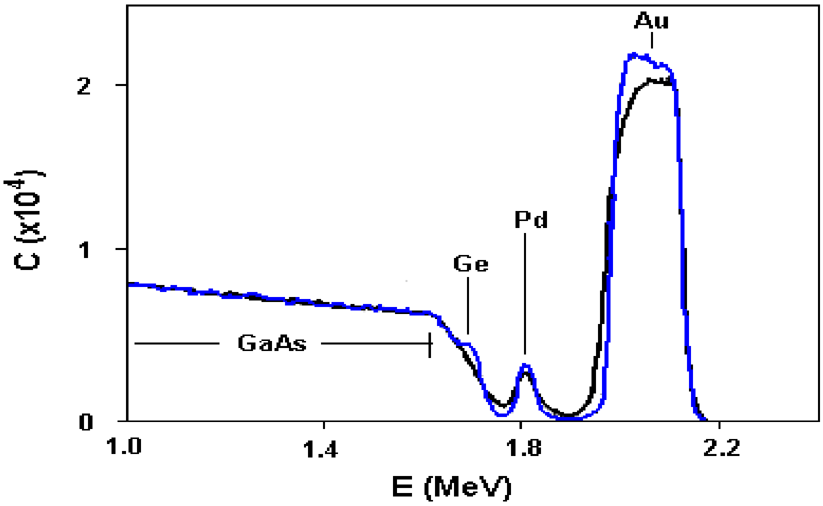

Figure 4. C vs. E: Rutherford 2.3 MeV $^4He^{++}$ backscattering spectra from the contact structure Au(100 nm)/Ge(40 nm)/Pd(10 nm). Upper (Au-rich region) line: as-deposited; lower line: after annealed at 180 ^{0}C for 1 h. Here, C and E denotes count and energy (in MeV) respectively.

The interfacial morphologies were studied. As observed, the deposited contacts are morphologically good with, e.g. good contact edges and small spread of the contacts, which make them suitable for the contacts of small areas, for example, for large-scale integration circuits. Here, ohmic contacts with low contact resistance are obtained by a process of low-temperature anneal. The low-temperature contacts can be suitable for the fabrication of proton-implanted stripe geometry diode lasers where the higher anneal temperature (~ 450 ^{0}C) of the more commonly used AuGe/Ni contact causes the proton damage to be partially removed, resulting in some current leakage [9,10]. In addition, these low-temperature annealed contacts result in a better surface for wire bonding and exhibit better stability under high-temperature atmospheric aging than do the conventional AuGe/Ni contacts. Thus, they may find use in a wide variety of devices requiring highly transparent contacts to *n*-type GaAs-based materials. The reproducibility and bondability were also studied and found to be good reproducible and strong wire bondable. Recently, these ohmic contacts (showing no schottky or photo-diode effects after illumination) have been used successfully in nonmagnetic spintronic device fabrication (Fig. 5), where the nonmagnetic contact materials were required [11].

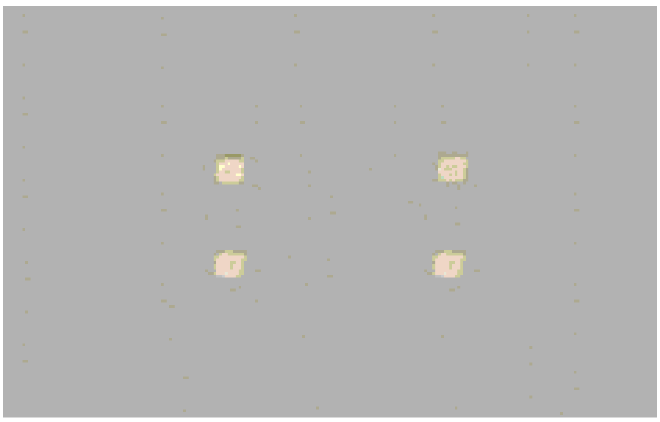

Figure 5. A photograph of the sample device (before wire bonding) in an expanded scale. The GaAs-based device contains longitudinal contacts spaced 200 μm apart and transverse contacts spaced 100 μm.

The nonmagnetic device used for the electrical detection of spin current and spin relaxation in GaAs was fabricated in a Hall geometry by depositing the structure Au(100 nm)/Ge(40 nm)/Pd(10 nm) and annealing it at T_a~180°C for 1 h in order to achieve the best reliability. The device contained longitudinal contacts spaced 200 μm apart and transverse contacts spaced 100 μm. A gold wire was bonded from the chip carrier to the centre of each contact.

Conclusions

Au(100 nm)/Ge(40 nm)/Pd(10 nm) contact structures on *n*-type GaAs were formed and studied. The contact resistivity ρ_c for the structures was assessed using transmission line model. The results showed that the structures under appropriate annealing period and temperature exhibit ohmic behaviour. It was found that ρ_c decreases with increasing annealing temperature up to ~180 ^{0}C and then it increases. The ρ_c was also found to decrease with increasing substrate-doping density. The compositional distribution in metallization of the structure Au/Ge/Pd was investigated by collecting the Rutherford 2.3 MeV $^4He^{++}$ backscattering spectra for the as-deposited structures and the structures after annealed. The compositional analysis supported the Au-Ge inter-diffusion mechanism of the contact formation. The formation mechanism was discussed in details.

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